1. The Projected GI Method and the Excited States of H_2.

2. A Superposition Principle for Siegert Resonant States.

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To Colonel Robert P. Knight
may he always get his man,
And to those who helped to see
That this one got away.

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ABSTRACT

The simplest orbital wavefunction that adequately describes the dissociation of the excited states of homonuclear diatomic molecules must involve a spatial symmetry projection operator. The use of such a wavefunction has been developed in detail and applied to the excited states of the hydrogen molecule. It was found that the advantages of an independent-particle description are enhanced considerably by spatial projection. The low-lying Σ states of H_2 are explained unambiguously and convincingly in terms of orbital character based on the model of the one-electron heteronuclear diatomics.

Recent experimental work in electron impact spectroscopy has illustrated that short-lived negative-ion resonances must play an important role. In an attempt to show that such resonances form a natural and complete characterization of the scattering process, the properties of the resonant states defined by Siegert have been investigated. In specific, a superposition principle for Siegert states was found, which provides a complete description of any quantum mechanical event involving a potential of finite range.

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PART 1

The Projected GI Method and the Excited States of H_2

INTRODUCTION

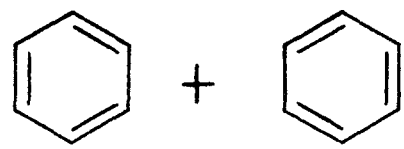
Spatial symmetry has played a dominant role in the study of quantum mechanical systems. The classification of states according to the representations of the appropriate group of symmetry transformations is a fundamental part of any student's introduction to quantum mechanical problems. The "elementary" illustrations of the hydrogen atom, hydrogen-molecular-ion, and the simple-harmonic-oscillator immediately come to mind. And even the stouthearted would falter before the numerous interesting many-particle problems (say, benzene, $Cr(CO)_6$, crystalline NaCl, ...) were it not for the simplification of classification by symmetry.

Indeed, the first step in the study of the electronic states of simple molecules is the determination of the term symbols (i.e., spin and spatial symmetries) of the states.[1] It is not at all surprising that the molecular symmetry be used to ease the construction of approximate descriptions of the molecular states. In specific, consider the simplest molecule, the H_2^+ molecular-ion. Its states form the basis of the molecular orbital description of homonuclear diatomics. The many-electron state is to be built up out of the one-electron orbitals. The result is called a configuration, as $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(1\pi_u)^4(3\sigma_g)^2$ for N_2. For polyatomics (such as benzene) a similar aufbau procedure applies, the model being the one-electron states with the same nuclear arrangement [giving $(1a_{1g})^2(1e_{1u})^4(1e_{2g})^4(1b_{1u})^2(2a_{1g})^2(2e_{1u})^4\ldots$, see Ref. 2].

The Hartree-Fock theory provides a scheme for finding an optimum[3] set of orbitals to be used to construct the many-electron

wavefunction. This method is tractable for (what seem at the moment) relatively large molecules (e.g., benzene[4]). The degree of success in explaining basic properties of the molecular states is nothing less than outstanding. Much of the success and practicability may be attributed directly to the molecular symmetrv and the use of this symmetry in the one-electron orbitals.[5] More specifically, the enormous contribution of molecular orbital theory to the spectroscopic study of electronic excited states has depended crucially on symmetry.

An alternate scheme of molecular structure places less emphasis on the nuclear arrangement, and less emphasis on the symmetry of the states. It corresponds more to the ordinary chemist's view of balls and sticks. The role of symmetry is mainly incidental. For saturated systems (say, cyclohexane), the conclusion is that all the bonds are identical. For unsaturated systems (say, benzene), there is more difficulty, but the resolution is informative. The simplest ball-and-stick (valence bond) model of benzene requires the "resonance" of two equivalent Kekulé structures:



This scheme of mdecular binding has served chemistry well. Recently, though, molecular orbital theory has acquired more of a following among organic chemists,[6] basically for its superior handling of excited states and symmetry. Correspondingly, theorists have become more interested in generalization of the valence bond techniques,[7]

basically for the superior description of bonding atoms into molecules, i.e., reactions.

Here we discuss a special generalized-valence-bond technique: spatial projection.[8] This means producing the known many-electron symmetries not by restrictions on the orbitals (as would be done in HF) but by adding together the various resonance forms (as for benzene above). The discussion will be generally restricted, for simplicity, to point symmetry groups with only nondegenerate representations. The development and application to two-electron systems and, in specific, to the excited states of the hydrogen molecule will be discussed in detail.

THE TECHNIQUES OF SPATIAL PROJECTION

A. The form of the wavefunction: The approximate many-electron wavefunction is chosen to have the following simplified form:

$$\Psi = P\psi_1\psi_2\cdots\psi_n , \tag{1}$$

where the ψ_i's are individual (perhaps generalized) spin orbitals. The projection operator is to provide the many-electron wavefunction with the known spin, spatial, and permutational symmetry.

This projection operator is frequently partitioned into components

$$P = P_{space}\cdot P_{permutation}\cdot P_{spin} \tag{2}$$

or

$$P = P_{space}\cdot P_{spin\ and\ permutation}.$$

Examples of combined spin and permutation projectors are provided by the G_i^γ operators, which are a sum of products. The principal topic of this chapter will be projected GI wavefunctions,

$$\Psi = P_{space}G_i^\gamma\,\varphi_1\varphi_2\cdots\varphi_n\,\alpha\beta\alpha\beta\cdots . \tag{3}$$

Suppose G is the abelian[9] point group of the molecule. The projection operator we want is then the Wigner projection operator[10] (onto, say, the λ^{th} representation):

$$P_{space} = O^\lambda = 1/g \sum_{R\epsilon G} \chi^\lambda(R^{-1})R , \tag{4}$$

where g is the order of the group and the $\chi^\lambda(R^{-1})$ is the character of the group operator R^{-1} for the λ^{th} representation. This projection operator is to be applied to the product of spatial orbitals, $\Phi = \varphi_1\varphi_2\cdots\varphi_n$.

Direct application would give

$$O^{\lambda}\Phi = 1/g \sum_{R \epsilon G} \chi^{\lambda}(R^{-1})[R\varphi_1][R\varphi_2]\cdots[R\varphi_n] . \tag{5}$$

This means keeping track of how to calculate $R\varphi_i$ and how to take a matrix element between Φ and $R\Phi$. The following tack may be simpler.

In molecular calculations, the orbitals are usually expanded over some finite set of basis functions,

$$\varphi_i = \sum_{\beta} C_i^{\beta} \eta_{\beta} . \tag{6}$$

These basis functions can be chosen to be, or transformed[11] to be, symmetry functions without loss of generality, and without much additional difficulty. This can be written as

$$\varphi_i = \sum_{\beta} C_i^{\beta} \eta_{\beta}(\mu) , \tag{7}$$

which means that $\eta_{\beta}(\mu)$ belongs to or transforms according to the μ^{th} representation of the spatial symmetry group G. As a consequence of this choice, $\eta_{\beta}(\mu)$ is an eigenfunction of the Wigner projectors [see Eq. (4)]

$$O^{\nu}\eta_{\beta}(\mu) = \eta_{\beta}(\mu) \cdot \delta_{\mu\nu} . \tag{8}$$

This suggests that we rewrite the n-electron spatial projector $O^{\lambda}(1\cdots n)$ as a sum of products of one-electron projectors. This can be done through the reciprocal[12] relation to Eq. (4),

$$R = \sum_{\mu} \chi^{\mu}(R) O^{\mu} , \tag{9}$$

substituting into Eq. (4) this gives

$$O^{\lambda}(1\,2\cdots n) = 1/g \sum_{R\in G} \chi^{\lambda}(R^{-1})R(1)R(2)\cdots R(n)$$

$$= 1/g \sum_{\mu_i} \sum_{R\in G} \chi^{\lambda}(R^{-1})\chi^{\mu_1}(R)\chi^{\mu_2}(R)\cdots\chi^{\mu_n}(R) \cdot O^{\mu_1}(1)O^{\mu_2}(2)\cdots O^{\mu_n}(n)\ . \tag{10}$$

To see how this works, we collect the last n-1 projectors together:

$$O^{\lambda}(1\,2\cdots n) = 1/g \sum_{\mu,\nu} \sum_{R} \chi^{\lambda}(R^{-1})\chi^{\mu}(R)\chi^{\nu}(R)O^{\mu}(1)O^{\nu}(2\,3\cdots n), \tag{11}$$

which can now be rewritten as

$$O^{\lambda}(1\,2\cdots n) = \sum_{\mu,\nu} (\lambda/\mu\nu)^2 O^{\mu}(1)O^{\nu}(2\,3\cdots n). \tag{12}$$

The collected term $O^{\nu}(2\,3\cdots n)$ can, of course, be broken down itself by Eq. (12) if desired. A very important property of this formula (12) is that the squared Clebsch-Gordan coefficients[13] $(\lambda/\mu\nu)^2$ take on only the values of 0 and 1, and for fixed λ and μ only one value of ν gives $(\lambda/\mu\nu)^2 \neq 0$.

It will be convenient at this point to set up some notation for the case of two electrons. Factoring out the spin part of the wavefunction gives[14]

$$\Psi^{\lambda}_{\text{space}} = \tfrac{1}{2} \sum_{\mu,\nu} (\lambda/\mu\nu)^2 O^{\mu}O^{\nu}\,[1 \pm (12)]\,\varphi_1(1)\varphi_2(2)\ . \tag{13a}$$

Each of the two orbitals is now broken up into its symmetry components

$$\varphi_i = \sum_{\mu} O^{\mu}\varphi_i = \sum_{\mu} \psi^{i}_{\mu}\ . \tag{13b}$$

So that Eq. (13a) becomes simply

$$\Psi^{\lambda}_{\text{space}} = \tfrac{1}{2} \sum_{\mu} [\psi^{1}_{\mu}\,\psi^{2}_{\gamma_\mu} \pm \psi^{2}_{\gamma_\mu}\,\psi^{1}_{\mu}\,]\ , \tag{13c}$$

where γ_μ is the uniquely defined representation that gives $(\lambda/\mu\gamma_\mu)^2 = 1$ (all others give zero). In the special case that λ is the totally symmetric representation, $\gamma_\mu = \mu$.

B. Density Matrices: The evaluation of the energy of the projected product approximate wavefunction, and the construction of iterative equations for its determination, will be much facilitated by the use of density matrices, defined in the sense of Goddard.[7h] The density matrix element $D^j_k(\mu)$ is defined as the coefficient of $\varphi^*_j(j)O^\mu(j)\varphi_k(j)$ in the expression[15] $\int \Phi^*(1\,2\cdots n)O_p\Phi(1\,2\cdots n)d\tau'_j$, where $O_p = O^\lambda(1\,2\cdots n)\cdot O_{ii}$. Similarly, $D^{ij}_{k\ell}(\mu)$ is the coefficient of the term $\varphi^*_i(i)\varphi^*_j(j)O^\mu(ij)\cdot\varphi_k(i)\varphi_\ell(j)$. The same technique may be used to define the higher-order density matrices.

As an example, consider the case of a two-electron singlet state, with symmetry ^1A. The spatial symmetry group is C_2.

$$O_{ii} = \tfrac{1}{2}(1 + (12))$$

$$O^A = \tfrac{1}{2}(1 + C_2) = [O^A(1)O^A(2) + O^B(1)O^B(2)]$$

$$\Phi^* O^A O_{ii}\Phi = \tfrac{1}{2}[\varphi^*_1\varphi^*_2 O^A(1)O^A(2)\varphi_1\varphi_2 + \varphi^*_1\varphi^*_2 O^B(1)O^B(2)\varphi_1\varphi_2 + \varphi^*_1\varphi^*_2 O^A(1)O^A(2)\varphi_2\varphi_1 + \varphi^*_1\varphi^*_2 O^B(1)O^B(2)\varphi_2\varphi_1]. \tag{14}$$

Therefore

$$D^1_1(A) = \tfrac{1}{2}\langle\varphi_2|O^A|\varphi_2\rangle \qquad D^1_1(B) = \tfrac{1}{2}\langle\varphi_2|O^B|\varphi_2\rangle$$

$$D^2_2(A) = \tfrac{1}{2}\langle\varphi_1|O^A|\varphi_1\rangle \qquad D^2_2(B) = \tfrac{1}{2}\langle\varphi_1|O^B|\varphi_1\rangle$$

$$D^1_2(A) = \tfrac{1}{2}\langle\varphi_2|O^A|\varphi_1\rangle = [D^2_1(A)]^*$$

$$D_2^1(B) = \tfrac{1}{2}\langle \varphi_2 | O^B | \varphi_1 \rangle = [D_1^2(B)]^*$$

$$D_{k\ell}^{ij}(\mu) = \tfrac{1}{2}\cdot(1-\delta_{k\ell})\cdot(1-\delta_{ij}) \qquad i,j,k,\ell = 1,2\ . \tag{15}$$

C. Expectation values: We are now prepared to calculate the expectation values of one- and two-electron operators, such as the overlap and the energy. The self-overlap of the approximate many-electron wavefunction, sometimes called the denominator or DENOM, is calculated simply as follows:

$$\text{DENOM} = \langle \Phi | O^\lambda O_{ii} | \Phi \rangle$$

$$= \sum_{k=1} \sum_{\ell=1} \sum_{\mu} \langle \varphi_k | O^\mu | \varphi_\ell \rangle D_\ell^k(\mu)\ . \tag{16}$$

The energy is to be calculated from the many-electron hamiltonian (written in atomic units):

$$H = \sum_i -\tfrac{1}{2}\nabla_i^2 + \sum_{i,m}(-Z_m/r_{im}) + \sum_{i\le j} 1/r_{ij} \tag{17a}$$

or

$$H = \sum_i T_i + \sum_i V_i + \sum_{i\le j} 1/r_{ij} \tag{17b}$$

kinetic energy; nuclear attraction; electron-electron repulsion

We need to calculate $\langle \Phi | HO^\lambda O_{ii} | \Phi \rangle / \text{DENOM}$. Now

$$\langle \Phi | HO^\lambda O_{ii} | \Phi \rangle = \sum_\mu \sum_{k\ell} \langle \varphi_k(1) | (T_1 + V_1) O^\mu(1) | \varphi_\ell(1) \rangle D_\ell^k(\mu)$$

$$\sum_\mu \sum_{k\ell pq}{}' \langle \varphi_k(1)\varphi_p(2) | \frac{1}{r_{12}} O^\mu(12) | \varphi_\ell(1)\varphi_q(2) \rangle D_{\ell q}^{kp}(\mu) \tag{18}$$

D. The Iterative Equations: To find the optimum orbitals to be used in the approximate many-electron wavefunction Eq. (2) we apply the ordinary Rayleigh-Ritz-Schrödinger variation condition,

$$\delta E = \langle \delta\Psi | H | \Psi \rangle - E\langle \delta\Psi | \Psi \rangle = 0 \ . \tag{19}$$

Since the only variations allowed are changes in the orbitals (or perhaps spin coupling), this becomes[16]

$$\delta E = \langle \delta\varphi_k \Phi'_k | HO_p | \Phi \rangle - E\langle \delta\varphi_k \Phi'_k | O_p | \Phi \rangle = 0 \ . \tag{20}$$

There are two kinds of techniques to be used in solving Eq. (20) for the optimum orbitals. These are called the 'Hamiltonian' and 'supermatrix' methods (see also Appendix III).

In the Hamiltonian method, each orbital is found as an eigenfunction of its own effective hamiltonian equation

$$H_k^v \varphi_k = \epsilon_k M_k \varphi_k \ , \tag{21}$$

where H_k^v is the hamiltonian for orbital φ_k, ϵ_k is its orbital energy, and M_k is the virtual metric operator for φ_k (further explanation is in Appendix III). This section will discuss how to construct the various projected integrals that are needed. For the hamiltonian we need integrals of the form $\langle \Phi_k^\alpha | HO_p | \Phi_k^\beta \rangle$, where we have set $O_p = O^\lambda \cdot O_{ii}$ and Φ_k^α means that orbital φ_k has been deleted from the orbital product Φ and basis function η_α has taken its place.

To evaluate these integrals, first define $g(12) = 1/(n-1)[T_1 + T_2 + V_1 + V_e] + 1/r_{12}$. Then

$$\langle \Phi_k^\alpha | HO_p | \Phi_k^\beta \rangle = \sum_\mu \sum_{pq} \{ \langle \eta_\alpha \varphi_p | gO^\mu | \eta_\beta \varphi_q \rangle D_{kq}^{kp}(\mu)$$

$$+ \langle \eta_\alpha \varphi_p | gO^\mu | \varphi_q \eta_\beta \rangle D_{qp}^{kp}(\mu) \}$$

$$\sum_{\mu,\nu} \sum_{pqrs} \{ \langle \eta_\alpha \varphi_p | gO^\mu | \varphi_q \varphi_r \rangle \langle \varphi_s | O^\nu | \eta_\beta \rangle D_{qrk}^{kps}(\mu \times \nu)$$

$$\langle \eta_\alpha | O^\nu | \varphi_q \rangle \langle \varphi_p \varphi_s | gO^\mu | \varphi_r \eta_\beta \rangle D_{qrk}^{kps}(\mu \times \nu)$$

$$+ \langle \eta_\alpha | O^\nu | \eta_\beta \rangle \langle \varphi_p \varphi_s | gO^\mu | \varphi_q \varphi_r \rangle D_{kqr}^{kps}(\mu \times \nu) \}$$

$$+ \sum_{\sigma,\mu,\nu} \sum_{pqrstu} \langle \eta_\alpha | O^\sigma | \varphi_s \rangle \langle \varphi_p | O^\nu | \eta_\beta \rangle \langle \varphi_q \varphi_r | gO^\mu | \varphi_t \varphi_u \rangle$$

$$\cdot D_{sktu}^{kpqr}(\mu \times \nu \times \sigma) \quad . \tag{22}$$

Finally, the virtual metric M_k is made from integrals of the form

$$\langle \Phi_k^\alpha | O_p | \Phi_k^\beta \rangle = \sum_\mu \langle \eta_\alpha | O^\mu | \eta_\beta \rangle D_k^k(\mu)$$

$$+ \sum_{\mu,\nu} \sum_{p,q} \langle \eta_\alpha | O^\nu | \varphi_q \rangle \langle \varphi_p | O^\mu | \eta_\beta \rangle D_{qk}^{kp}(\mu \times \nu) \quad . \tag{23}$$

Certain simplifications of these equations obtain in practice, such as the fact that $\langle \eta_\alpha(\mu) | O^\nu | \eta_\beta(\sigma) \rangle = \delta_{\alpha\beta} \delta_{\mu\nu} \delta_{\nu\sigma}$ if the basis functions are chosen to be orthonormal symmetry functions. These simplifications will not be discussed in detail here (see also Appendix II).

For the supermatrix technique one needs the very similar integrals: $\langle \Phi_k^\alpha | HO_p | \Phi_\ell^\beta \rangle$, $\langle \Phi_k^\alpha | HO_p | \Phi \rangle$, $\langle \Phi_{k\ell}^{\alpha\beta} | HO_p | \Phi \rangle$ and the same repeated with the H removed. These are to be calculated with formulas along the same lines as those for the hamiltonian method above.

E. Uniqueness of the orbitals: In solving the Hartree-Fock (HF) equations, it is well-known that the orbitals are not uniquely determined by optimization of the energy alone. In fact, the HF wavefunction

$$\Psi_{HF} = \mathcal{A}\, \varphi_1\varphi_1\varphi_2\varphi_2 \cdots \varphi_{n/2}\varphi_{n/2}\alpha\beta\alpha\beta\cdots\alpha\beta \tag{24}$$

is unchanged (except by a multiplicative factor) for arbitrary linear transformations of the orbitals amongst themselves. This means that the optimization of the energy [Eq. (20)] cannot specify which of these many linear combinations should be used.

The HF technique for unique specification of the orbitals is also well-known. First the orbitals are chosen to be normalized and mutually orthogonal. This restricts further linear transformations to be unitary. Finally the 'orbital energy matrix' is diagonalized. So that the orbitals are now completely determined except for irrelevant phase factors. The HF procedure will be further discussed below as an example and special case of the general techniques for removing arbitrariness.

The original product of orbitals, $\Phi = \varphi_1\varphi_2\cdots\varphi_n$, in general, will not have the desired many-electron symmetry. If it did, the projection operator $O^\lambda O_{ii}$ would be superfluous. This means that projection $O^\lambda O_{ii}\cdot\Phi$ must necessarily discard some of the original components of the orbital product. This can be written as

$$\Phi = \sum_\Gamma O^\Gamma \Phi = \sum_\Gamma \Phi_\Gamma\,, \tag{25}$$

where the sum over Γ is a sum over the representations of G × spin.

As an example, consider the two-electron case with symmetry group C_2. The representations (Γ) are then ^1A, ^3A, ^1B, ^3B. Equation (25) then becomes

$$\Phi = \varphi_1\varphi_2 = \Phi_{^1A} + \Phi_{^3A} + \Phi_{^1B} + \Phi_{^3B} . \tag{26}$$

Now if the desired symmetry is, say, ^1A, then the wavefunction that is solved for is $\Phi_{^1A} = O^{^1A}\Phi$. The problem of the nonuniqueness of the orbitals can now be stated. When there exist ways of changing the orbitals such that the projected wavefunction $O^{\lambda}O_{ii}\Phi$ is not changed, but any of the other terms of Eq. (25) are changed, then the orbitals cannot be specified by optimization of the energy alone.

Consider the even simpler example of solving for a two-electron triplet state with no spatial symmetry. The product $\Phi = \varphi_1\varphi_2$ is decomposed according to Eq. (25) as

$$\begin{aligned} \Phi &= \Phi_1 + \Phi_3 \\ &= \tfrac{1}{2}[\varphi_1(1)\varphi_2(2) + \varphi_2(1)\varphi_1(2)] + \tfrac{1}{2}[\varphi_1(1)\varphi_2(2) - \varphi_2(1)\varphi_1(2)] . \end{aligned} \tag{27}$$

singlet triplet

The triplet component is the one we are after. Now suppose we try to change orbital φ_1 by adding some φ_2 to it

$$\bar{\varphi}_1 = \varphi_1 + z\,\varphi_2 . \tag{28}$$

Then Eq. (27) becomes

$$\begin{aligned} \bar{\Phi} &= \tfrac{1}{2}[\bar{\varphi}_1\varphi_2 + \varphi_2\bar{\varphi}_1] + \tfrac{1}{2}[\bar{\varphi}_1\varphi_2 - \varphi_2\bar{\varphi}_1] \\ &= \tfrac{1}{2}[\varphi_1\varphi_2 + \varphi_2\varphi_1 + 2z\,\varphi_2\varphi_2] + \tfrac{1}{2}[\varphi_1\varphi_2 - \varphi_2\varphi_1] . \end{aligned} \tag{29}$$

So the triplet component did not change but the singlet did; hence the parameter z must be found by some other criterion: the criterion to use in this simple case is apparent; it is built into our intuitions from repeated application; the orbitals φ_1 and φ_2 are just chosen to be orthogonal. This gives

$$\langle \varphi_2 | \varphi_1 + z\,\varphi_2 \rangle = 0$$

or

$$z = \frac{-\langle \varphi_1 | \varphi_2 \rangle}{\langle \varphi_2 | \varphi_2 \rangle} \quad . \tag{30}$$

For a more complicated case, a more general criterion will be needed.

1. Maximizing the denominator: A better focus on the problem can be had by examining the relative magnitudes of the singlet and triplet components in the above example [Eq. (29)]

$$\frac{\text{triplet}}{\text{singlet}} = \frac{\langle \varphi_1 | \varphi_1 \rangle \langle \varphi_2 | \varphi_2 \rangle - |\langle \phi_1 | \varphi_2 \rangle|^2}{\langle \varphi_1 | \varphi_1 \rangle \langle \varphi_2 | \varphi_2 \rangle + |\langle \varphi_1 | \varphi_2 \rangle|^2 + 2z \langle \varphi_2 | \varphi_2 \rangle \langle \varphi_1 | \varphi_2 \rangle + z^2 \langle \varphi_2 | \varphi_2 \rangle^2} \quad . \tag{31}$$

Suppose we add a lot of φ_2 to φ_1, i.e., z is to be very large. That means that the triplet/singlet ratio will become very small. The orbital product will be mostly singlet, while the projected wavefunction is to be a triplet. The projection operator is throwing away most of the orbitals. This is very bad since we want to interpret the many-electron wavefunction in terms of the orbitals. The reliability of the orbital scheme of interpretation depends on the closeness of the simple product of the orbitals $\Phi = \varphi_1 \varphi_2 \cdots \varphi_n$, and the final many-electron wavefunction $\Psi = P\Phi$.

The conclusion is,that the criterion to be used to specify the orbitals will be,that the overlap (i.e., resemblance) of the orbital product with the projected wavefunction $\langle \Phi | P\Phi \rangle$ be a maximum. This overlap is just the denominator as defined in Eq.(16), and so the orbital selection procedure is called maximizing the denominator. This maximization must, of course, be done while holding the orbital product (and hence the individual orbitals) to be normalized. So we maximize $\langle \Phi | P | \Phi \rangle / \langle \Phi | \Phi \rangle$.

In the simple example above,

$$\text{DENOM}(z) = \frac{\frac{1}{2}[\langle \varphi_1 | \varphi_1 \rangle \langle \varphi_2 | \varphi_2 \rangle - |\langle \varphi_1 | \varphi_2 \rangle|^2]}{\langle \varphi_1 | \varphi_1 \rangle \langle \varphi_2 | \varphi_2 \rangle + 2z \langle \varphi_1 | \varphi_2 \rangle \langle \varphi_2 | \varphi_2 \rangle + z^2 |\langle \varphi_1 | \varphi_2 \rangle|^2} . \quad (32)$$

Now maximizing, which is just solving (d/dz)DENOM(z) = 0, gives exactly Eq.(30).

Actually the problem is not quite solved. Even after the orbitals are orthogonal, unitary transformations may yet be performed amongst the orbitals with no change in the many-electron wavefunction and hence no change in the energy or the denominator. As mentioned before, the resolution is well-known for the above simple case. The diagonalization of an orbital energy or Lagrange multiplier matrix will produce completely determined orbitals.

2. Orbital energies: A rather backward-seeming definition of the orbital energy is used here, but it appears to describe the physical situation.[17] Koopmans[18] was one of the first to characterize the diagonal Hartree-Fock Lagrange multipliers as approximate vertical

ionization energies. This identification was an important support for attributing physical significance to the individual orbitals. In this vein we define the orbital energy ϵ_n for the last (highest) orbital through the calculated vertical ionization energy

$$\epsilon_n = E_n - E_{n-1} \,, \tag{33}$$

where E_n is the total energy of the full n-electron wavefunction, E_{n-1} is the energy of the n-1 electron wavefunction obtained by merely deleting φ_n.

Following Koopmans, we seek to make ϵ_n as close as possible to the ionization energy by permitting transformations of the orbitals amongst themselves that do not change the energy, E_n (or the denominator). This means finding the best approximation to the n-1 electron state (lowest E_{n-1}) within the allowable rearrangements of the orbitals. This technique will then define what orbital is to be deleted, i.e., φ_n. To specify the other orbitals (and orbital energies) we repeat the procedure for φ_{n-1} with φ_n fixed.[19]

For (closed-shell) Hartree-Fock, this just means that all of the orbitals should be eigenfunctions of one Hartree-Fock hamiltonian,

$$H_{HF} = h + \sum_i (2J_i - K_i) \tag{34}$$

$$H_{HF}\varphi_i = \epsilon_i \varphi_i \quad . \tag{35}$$

3. Two electrons--the Denominator: "(x, 1/x)" transformations.

First consider λ to be the totally symmetric representation. From Eq. (13c)

$$\Psi = \tfrac{1}{2} \sum_{\mu} [\psi^1_\mu \psi^2_\mu \pm \psi^2_\mu \psi^1_\mu] \ . \tag{36}$$

We can easily see that if we make the replacements of

$$\begin{aligned} &\psi^1_\mu \text{ by } x_\mu \psi^1_\mu \\ \text{and} \qquad & \\ &\psi^2_\mu \text{ by } 1/x_\mu \psi^2_\mu \ , \end{aligned} \tag{37}$$

where x_μ is any number (one for each representation μ). Then Ψ is unchanged,

$$\begin{aligned} \Psi' &= \tfrac{1}{2} \sum_{\mu} [(x_\mu \psi^1_\mu)(1/x_\mu \psi^2_\mu) \pm (1/x_\mu \psi^2_\mu)(x_\mu \psi^1_\mu)] \\ &= \Psi \ . \end{aligned} \tag{38}$$

This transformation is called a "(x, 1/x)" transformation.

To see what the (x, 1/x) transformation does, we look at the example of ^1A projection for the group C_2. Then

$$\Psi = \tfrac{1}{2} [\psi^1_A \psi^2_A + \psi^1_B \psi^2_B + \psi^2_A \psi^1_A + \psi^2_B \psi^1_B]$$

where

$$\varphi_1 = \psi^1_A + \psi^1_B \ , \qquad \varphi_2 = \psi^2_A + \psi^2_B \ . \tag{39}$$

The transformation to be examined is

$$\begin{aligned} \varphi'_1 &= x \, \psi^1_A + \psi^1_B \\ \varphi'_2 &= 1/x \, \psi^2_A + \psi^2_B \ . \end{aligned} \tag{40}$$

Now if x is chosen to be very large, then each of the orbitals is

dominated by one of its components

$$\varphi'_1 \sim \psi^1_A$$
$$\varphi'_2 \sim \psi^2_B \quad . \tag{41}$$

The orbital product therefore becomes $\Phi \sim \psi^1_A \psi^2_B$, which is of B symmetry, which is not the symmetry we wanted.

This can be put more precisely through the use of the decomposition Eq. (26), wherewith

$$\Phi' = \varphi'_1 \varphi'_2 = \Phi'_{1A} + \Phi'_{3A} + \Phi'_{1B} + \Phi'_{3B} \, . \tag{42}$$

Now

$$\Phi'_{1A} = \Psi' = \Psi = \tfrac{1}{2}[\psi^1_A\psi^2_A + \psi^1_B\psi^2_B + \psi^2_A\psi^1_A + \psi^2_B\psi^1_B] \tag{43a}$$

$$\Phi'_{3A} = \Phi_{3A} = \tfrac{1}{2}[\psi^1_A\psi^2_A + \psi^1_B\psi^2_B - \psi^2_A\psi^1_A - \psi^2_B\psi^1_B] \tag{43b}$$

$$\text{and } \Phi'_{1,3B} = \tfrac{1}{2}[x(\psi^1_A\psi^2_B \pm \psi^2_B\psi^1_A) + 1/x(\psi^1_B\psi^2_A \pm \psi^2_A\psi^1_B)] \, . \tag{43c}$$

So that the totally symmetric components $\Phi_{1,3A}$ are independent of x, but the antisymmetric components $\Phi_{1,3B}$ are not. Maximization of the denominator will determine the value of x that should be used. This procedure is described in detail in Appendix IV. After the denominator is maximized, there are no undetermined unitary transformations. The orbitals are completely defined.

The maximization as described in Appendix IV gives the following interesting final result:

$$\langle \psi^1_\mu | \psi^1_\mu \rangle = \langle \psi^2_\mu | \psi^2_\mu \rangle \tag{44}$$

for the optimum orbitals.

Again for the group C_2 we look at a nonsymmetric representation, say, ^1B

$$\Psi = O^{^1B}\varphi_1\varphi_2 = \tfrac{1}{2}[(\psi_A^1\psi_B^2 + \psi_B^2\psi_A^1) + (\psi_B^1\psi_A^2 + \psi_A^2\psi_B^1)] \ . \tag{45}$$

Now the replacement of φ_1 by $x\,\psi_A^1 + \psi_B^1$ and φ_2 by $\psi_A^2 + 1/x\ \psi_B^2$ produces no change in the projected many-electron wavefunction (45). The optimization of this case is also worked out in Appendix IV. The final result being

$$\begin{aligned} \langle \psi_A^1 | \psi_A^1 \rangle &= \langle \psi_B^2 | \psi_B^2 \rangle \\ \langle \psi_B^1 | \psi_B^1 \rangle &= \langle \psi_A^2 | \psi_A^2 \rangle \ . \end{aligned} \tag{46}$$

But now this is not the only kind of transformation. So more work is needed before the orbitals are determined.

"Shape" transformations:

Dunning[20] found that for nonsymmetric singlet states [such as shown in Eq. (45)] the "shape" transformation

$$\varphi_1 \rightarrow \varphi_1 + z[\psi_A^2 - \psi_B^2] \tag{47}$$

does not affect the many-electron wavefunction. The nature of this transformation is more easily seen by examining the orbitals as follows. We call φ_1 instead φ_1^L (since it might be mostly on the left of the molecule) and φ_2 as φ_2^R (mostly on the right?). Then the natural definition of φ_1^R and φ_2^L would be

$$\begin{aligned} \varphi_1^R &= C_2\varphi_1^L = C_2[\psi_A^1 + \psi_B^1] = \psi_A^1 - \psi_B^1 \\ \varphi_2^L &= C_2\varphi_2^R = C_2[\psi_A^2 + \psi_B^2] = \psi_A^1 - \psi_B^2 \ . \end{aligned} \tag{48}$$

So now the replacement (47) is just transforming the orbitals after putting them both on the same center,

$$\varphi_1^L \rightarrow \varphi_1^L + z\,\varphi_2^L \,. \tag{47'}$$

The optimization of the parameter z (as further discussed in Appendix IV) gives

$$\langle \varphi_1^L | \varphi_2^L \rangle = 0 \tag{49}$$

for the optimum z. This means that we have orthogonalized the "shapes" of the orbitals φ_1 and φ_2. In practice, this means, for example in the case of H_2, that when a $^1\Sigma_u^+$ state dissociates the two orbitals must not have the same character. An allowed dissociation would be a 1s on the left hydrogen and a 2p on the right. Their shapes are orthogonal. Dissociation to two 1s atoms is forbidden since their shapes are identical. In fact, the many-electron wavefunction for that state vanishes

$$\Psi = [\varphi_1^L\varphi_2^R + \varphi_2^R\varphi_1^L - \varphi_1^R\varphi_2^L - \varphi_2^L\varphi_1^R] = 0 \tag{50}$$

if $\varphi_1^L = 1s_L$ and $\varphi_2^R = 1s_R$, so that $\varphi_1^L = \varphi_2^L$.

For the singlet, non-symmetric case, even after the denominator is maximized both for (x, 1/x) and shape transformations, there remain "unitary" shape transformations. The final resolution must come from an orbital energy matrix.

4. Two electrons - the orbital energies: The idea of finding orbital energies (as explained above) is basically to make the ionization energy (which is in this case $\epsilon_2 = E_2 - E_1$) as small as possible, which is the

same as making the core of the n-electron system be as close as possible to the n-1 electron wavefunction of the ion.

In the ^1B case above the transformation that is yet to be defined is

$$\begin{aligned} \varphi_1^L \rightarrow \bar{\varphi}_1^L &= \cos\theta\ \varphi_1^L + \sin\theta\ \varphi_2^L \\ \varphi_2^R \rightarrow \bar{\varphi}_2^R &= -\sin\theta\ \varphi_1^R + \cos\theta\ \varphi_2^R\ . \end{aligned} \tag{51}$$

If DENOM has been maximized, then the shapes are already orthogonal and this transformation (51) leaves the wavefunction, Ψ and DENOM unchanged. So we write down ϵ_2,

$$\epsilon_2 = E_2 - \langle \bar{\varphi}_1^L | h | \bar{\varphi}_1^L \rangle$$

$$\begin{aligned} \epsilon_2(\theta) = E_2 &- \cos^2\theta \langle \varphi_1^L | h | \varphi_1^L \rangle - \sin^2\theta \langle \varphi_1^L | h | \varphi_1^L \rangle \\ &+ 2 \sin\theta \cos\theta \langle \varphi_1^L | h | \varphi_1^L \rangle\ . \end{aligned} \tag{52}$$

The only step remaining is to maximize ϵ_2 with respect to θ, i.e.,

$$d\epsilon_2/d\theta = +\sin 2\theta [h_{11} - h_{22}] + 2 \cos 2\theta\ h_{12} \tag{53a}$$

so

$$\text{ctn}\ 2\theta = (h_{22} - h_{11})/2h_{12}\ . \tag{53b}$$

Now the orbitals are determined. Once again a complete description of the maximization of the denominator and the diagonalization of the orbital energy matrix for two electrons and general abelian groups is given in Appendix IV. Appendix V discusses this same problem for spin projection of generalized spin orbitals.

RESULTS - H_2

A. Introduction: The electronic states of the hydrogen molecule form a simple quantum mechanical system, at least compared with other molecules. For a molecular model as successful as the molecular-orbital/Hartree-Fock theory has been, hydrogen should be its most conspicuous triumph. It is not.

The molecular orbital (MO) theory for H_2 begins with the orbital correlation diagram,[21] based on the states of H_2^+, as shown in Fig. 1. The states of H_2 are formed simply by placing one or two electrons in the various molecular orbitals. The low-lying Σ states would then be described as follows (in order of increasing energy):

$$\begin{aligned} (1\sigma_g)^2 &\rightarrow 1\,^1\Sigma_g^+ \\ 1\sigma_g 1\sigma_u &\rightarrow 1\,^3\Sigma_u^+,\ 1\,^1\Sigma_u^+ \\ 1\sigma_g 2\sigma_g &\rightarrow 1\,^3\Sigma_g^+,\ 2\,^1\Sigma_g^+, \end{aligned} \tag{54}$$

where the states to be derived from each configuration are listed on the right. This simple model gives a surprisingly good description of the character of the states near equilibrium internuclear separation. The order of the states in Eq. (54) is correctly predicted; the appearance of the Rydberg series, such as $(1\sigma_g)(n\sigma_g)$, is explained; and the lowest triplet is predicted to be unstable. But certain problems remain. Since we are interested in the electronic structure not only at nuclear equilibrium but we also want to construct, analyze, and explain the effective potentials for nuclear motion. With only the one exception of the lowest triplet, the simple MO ideas are unable to describe adequately the

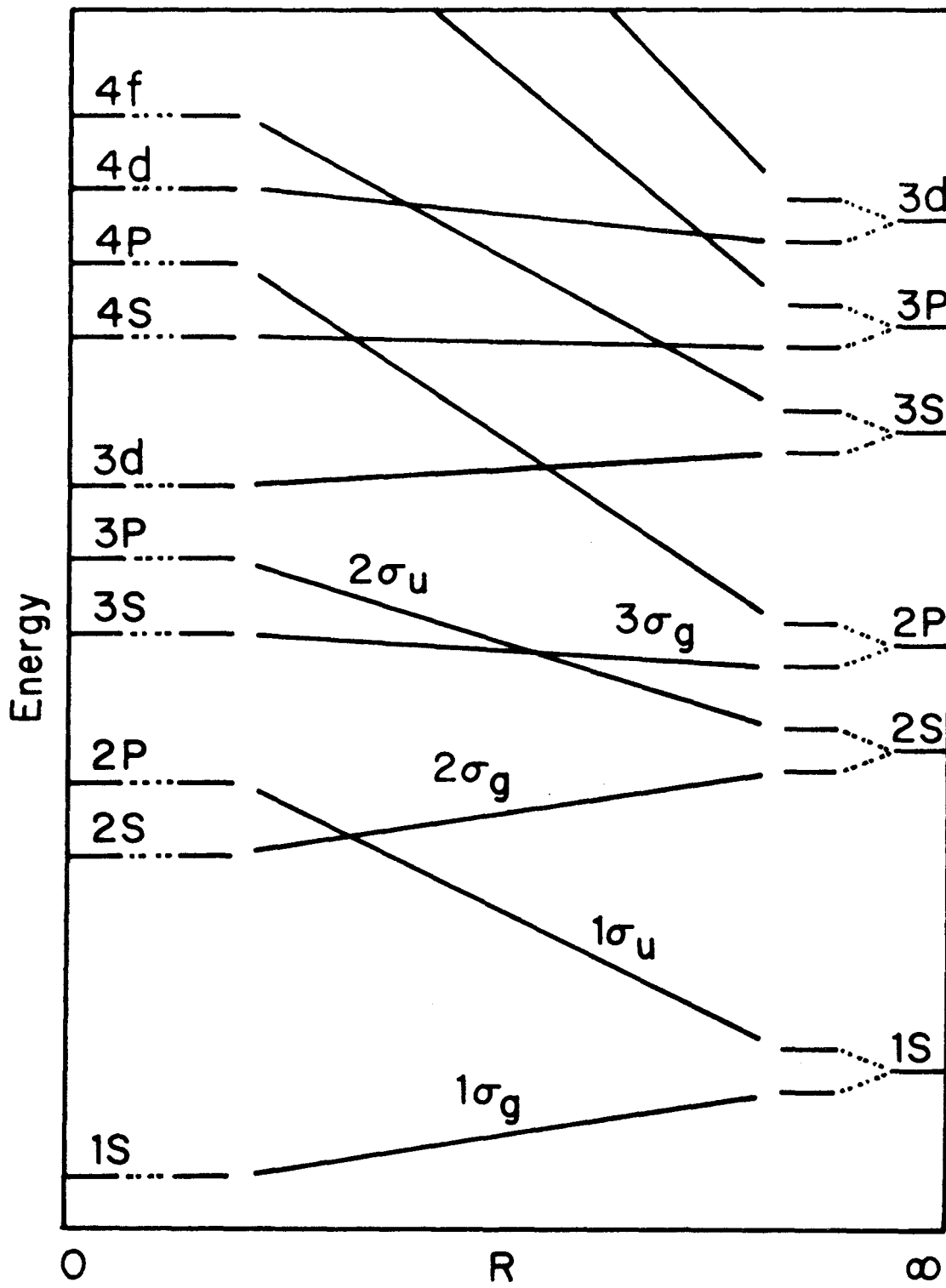


Fig. I. MO Correlation Diagram

potential curves and dissociation products. This is particularly important, since much of molecular spectroscopy is the study of the potential curves.

First consider the ground state, which was $(1\sigma_g)^2$. The correlation diagram suggests dissociation into ground state atoms, $1\sigma_g \rightarrow 1s_L + 1s_R$. This means that the total wavefunction becomes

$$\Psi \rightarrow [(1s_L 1s_R + 1s_R 1s_L) + (1s_L 1s_L + 1s_R 1s_R)](\alpha\beta - \beta\alpha) \qquad (55)$$

covalent ionic

(ignoring normalization), where $1s_L$ and $1s_R$ are H 1s orbitals on the left and right, respectively. The covalent term is the wavefunction that describes two ground-state hydrogen atoms very far apart. The MO description, even with self-consistent (Hartree-Fock) optimization of the orbitals, fails to account correctly for the dissociation, and therefore most of the potential curve. The difficulty is the high energy of the unavoidable ionic term (off by almost 8 eV at large R).

More seriously, excited configurations are predicted to correlate with the wrong separated-atom limits. For example, at large R the $1\sigma_g$ and $1\sigma_u$ orbitals of H_2^+ have the form

$$\begin{aligned} 1\sigma_g &= 1s_L + 1s_R \\ 1\sigma_u &= 1s_L - 1s_R \,. \end{aligned} \qquad (56)$$

Thus the $^3\Sigma_u^+$ and $^1\Sigma_u^+$ states constructed from configurations $1\sigma_g 1\sigma_u$ would be expected to dissociate into hydrogen atoms, each in the ground state. However, the only two-electron states that can be constructed

from two ground-state H atoms are the $^1\Sigma_g^+$ and $^3\Sigma_u^+$ states. In fact, the lowest $^1\Sigma_u^+$ state dissociates to one H atom in the 1s state and one H atom in an n = 2 state (2s or 2p).

The types of difficulties and inconsistencies mentioned above occur quite generally and become even more troublesome for larger molecules. But in spite of all this, H_2 should remain a simple system. The attractive idea of putting the electrons in one at a time should be salvagable. One single aspect of the MO correlation diagram is causing most of the trouble. The hydrogen molecule is homonuclear. It was more than natural that the homonuclear ion H_2^+ should have been chosen as the model. The nuclear symmetry was frequently used in the correlation diagram, and in classifying the one-electron orbitals and the two-electron states. This symmetry is usually treated as a gift, an obvious simplification in describing the states. I contend that the symmetry is a trap.

This brings us back to the start. Since we want to ensure that our description behaves correctly at large R, we will first examine the known limiting forms for R = ∞. The lowest states must involve a hydrogen 1s orbital on the left and right, which yields the spatial wavefunctions,

$$1s_L 1s_R + 1s_R 1s_L \tag{57a}$$

$$1s_L 1s_R - 1s_R 1s_L \,, \tag{57b}$$

leading to $^1\Sigma_g^+$ and $^3\Sigma_u^+$ symmetries respectively when combined with a spin function and antisymmetrized. We will denote these states as:

$$^1\Sigma_g^+ \qquad \boxed{1s_L 1s_R} \tag{58a}$$

$$^3\Sigma_u^+ \qquad \begin{vmatrix} 1s_L \\ 1s_R \end{vmatrix} \tag{58b}$$

where orbitals in the same row are understood to be symmetrically combined [as in (58a)] and orbitals in the same column are understood to be antisymmetrically combined [as in (58b)]. At large R the other states of the system must involve excited states of the atoms, the lowest of which would be one H atom in the 1s state and one in an n = 2 state (2s or 2p). Using ϕ_b = 2s and ϕ_a = 1s, we obtain the following four two-electron wavefunctions:

$$^1\Sigma_g^+ \qquad \boxed{\phi_{aL}\phi_{bR}}\ g \equiv \boxed{\phi_{aL}\phi_{bR}} + \boxed{\phi_{aR}\phi_{bL}} \tag{59a}$$

$$^1\Sigma_u^+ \qquad \boxed{\phi_{aL}\phi_{bR}}\ u \equiv \boxed{\phi_{aL}\phi_{bR}} - \boxed{\phi_{aR}\phi_{bL}} \tag{59b}$$

$$^3\Sigma_g^+ \qquad \begin{vmatrix} \phi_{aL} \\ \phi_{bR} \end{vmatrix}\ g \equiv \begin{vmatrix} \phi_{aL} \\ \phi_{bR} \end{vmatrix} + \begin{vmatrix} \phi_{aR} \\ \phi_{bL} \end{vmatrix} \tag{59c}$$

$$^3\Sigma_u^+ \qquad \begin{vmatrix} \phi_{aL} \\ \phi_{bR} \end{vmatrix}\ u \equiv \begin{vmatrix} \phi_{aL} \\ \phi_{bR} \end{vmatrix} - \begin{vmatrix} \phi_{aR} \\ \phi_{bL} \end{vmatrix} . \tag{59d}$$

These wavefunctions are just spatially projected orbital products as described above. Now with one H atom excited, the excitation can be either on the left or the right, leading to the two terms in each of the wavefunctions (59). The same procedure applies to the higher excited states.

The wavefunctions in (58) and (59) were constructed using atomic orbitals and are the exact molecular states for R = ∞. For finite R the exact wavefunctions can no longer be written in such simple forms;

however, we will consider approximate wavefunctions at finite R where the form of the wavefunction is taken as in (58) or (59) but in which the orbitals (ϕ_a and ϕ_b) are solved for variationally as a function of the internuclear distance rather than taken as atomic orbitals.

We will find that this projected generalized valence bond technique will provide a consistent description of the low-lying states of H_2. Further, this method permits and suggests that any state be built up out of its constituent orbitals, and that these orbitals may be described by a one-electron model--that is, an orbital correlation diagram.

B. The Calculations: The original objective when the herein reported calculations were done was rather limited. It was basically twofold. The question of what constituted a "valence" state was to be investigated. Specifically, the B $^1\Sigma_u^+$ (first $^1\Sigma_u^+$) state of H_2 had been called a valence state since it was to be made out of 1s orbitals, i.e., $1\sigma_g 1\sigma_u$. Recognizing that the problem in the dissociation of this state could be solved no more simply than by spatial projection, spatial projection itself became of interest.

The basis set chosen was made from 32 gaussian primitive functions, (10s, 6p), on each center contracted into 16 functions as shown in Table I.

TABLE I. The 16 BF H_2 basis, (10s, 6p) gaussian primitives, [5s, 3p] contracted functions on each center.

Orbital Exponent	Contraction Coefficient	
82.4736	0.00688397	first s
12.3983	0.05205669	
2.83924	0.25325049	
0.81472	0.76848733	
0.27184	1.0	second s
0.09948	1.0	third s
4.6935	-0.01716550	fourth s
0.5827	-0.11769463	
0.0427	1.03642546	
0.0165	1.0	fifth s
2.44001	0.33711392	first p
0.56748	0.77640215	
0.7338	0.03893322	second p
0.1742	0.26990651	
0.0557	0.78413778	
0.0202	1.0	third p

The first three s functions and the first p function were taken from the H_2 calculations of R. C. Ladner.[22] The last two s functions and the last two p's were taken from Huzinaga's[23] expansion of 2s and 2p Slater functions with orbital exponent of $1/n = 1/2$. Since initially only $n = 1$ and $n = 2$ H_2 states were to be studied, this basis should have been (and was) adequate. For reference, Table II gives a description of the hydrogen atom in this basis.

TABLE II. Hydrogen atom in the 16 BF basis (in atomic units).

	1s	2s	2p
E	-0.499905	-0.124927	-0.124956
V/2E	1.000351	--	1.000956
C_1	0.308373	0.087098	0.001863
C_2	0.491603	0.227168	0.676341
C_3	0.295503	0.303389	0.415377
C_3	0.023548	-0.443745	
C_4	0.000873	-0.791773	

An attempt to describe the 3s and 3p states of hydrogen gave energies of -0.2754 and -0.3239, respectively, compared with the correct -0.05555. The 16 BF basis will be expected to do poorly for $n = 3$ states.

In this basis optimum projected wavefunctions for the lowest three $^1\Sigma_g^+$ states, and the lowest two states for each of the symmetries $^1\Sigma_u^+$, $^3\Sigma_g^+$, $^3\Sigma_u^+$ were found for a variety of internuclear distances from

R = 0.8 to R = 16 atomic units. The resulting total energies are reported in Table III, and plotted in Fig. 2. In Table IV we have the orbital energies ϵ_b for the outer orbital. The orbital coefficients are given in Appendix VI.

As will be more fully illustrated below, H_2 turned out to be a more interesting molecule than was originally thought. The higher states were more complicated than expected. To look at these higher states and to verify that the highest states reported in Table III were adequately described, three distances were redone with a slightly larger basis. The idea was to put in more diffuse functions to describe n = 3 states as well. A basis of 56 Gaussian primitives was selected, (11s, 8p, 3d), on each center. The old 16 BF basis was just increased by adding 1s, 2p, and 3d's on each center. This was first contracted to 26 functions [6s, 4p, 1d] that gave H-atom energies of -0.499905, -0.124935, -0.055484, -0.124960, -0.055486, and -0.055492 for the 1s, 2s, 3s, 2p, 3p, and 3d levels, respectively. Finally, the basis was further contracted to 18 basis functions. The tightest contracted function at each of the distances done (R = 2, 3, 4 a_0) was taken to be the φ_a (inner) orbital from the 16 BF calculation on the $2\ ^1\Sigma_u^+$ state. The total energies of the higher states are reported in Table V.

TABLE III. PGVB H_2 total energies in the 16 BF Basis (in a.u.)

R	$1\,^1\Sigma_g^+$	$2\,^1\Sigma_g^+$	$3\,^1\Sigma_g^+$	$1\,^1\Sigma_u^+$	$2\,^1\Sigma_u^+$	$1\,^3\Sigma_g^+$	$2\,^3\Sigma_g^+$	$1\,^3\Sigma_u^+$	$2\,^3\Sigma_u^+$
∞	-0.99981	-0.62486	-0.62483	-0.62486	-0.62483	-0.62486	-0.62483	-0.99981	-0.62486
16	-0.99981	-0.62486	-0.62463	-0.62518	-0.62486	-0.62513	-0.62483	-0.99981	-0.62483
12	-0.99981	-0.62664	-0.62456	-0.62736	-0.62507	-0.62536	-0.62464	-0.99981	-0.62473
10	-0.99982	-0.63381	-0.62443	-0.63475	-0.62508	-0.62555	-0.62379	-0.99981	-0.62457
8	-0.99984	-0.65143	-0.62426	-0.65255	-0.62560	-0.62612	-0.62041	-0.99981	-0.62423
6	-1.00044	-0.67947	-0.62527	-0.68152	-0.62559	-0.62956	-0.61243	-0.99951	-0.62351
5	-1.00284	-0.69340	-0.62971	-0.69957	-0.62499	-0.63764	-0.60913	-0.99821	-0.62467
4	-1.01349	-0.69446	-0.64331	-0.71831	-0.62682	-0.65815	-0.61278	-0.99253	-0.63453
3.5	-1.02700	-0.68466	-0.65210	-0.72743	-0.63232	-0.67472	--------	-0.98501	-0.64550
3	-1.04993	-0.68563	-0.64595	-0.73625	-0.64237	-0.69523	-0.63263	-0.97056	-0.65992
2.5	-1.08374	-0.70156	-0.64791	-0.74331	-0.65411	-0.71719	-0.64648	-0.94360	-0.67451
2.0	-1.12526	-0.71422	-0.65419	-0.74282	-0.65948	-0.73334	-0.65429	-0.89471	-0.68089
1.5	-1.15768	-0.70014	-0.63346	-0.71472	-0.63661	-0.72225	-0.63411	-0.80707	-0.65576
1.4	-1.15884	-0.68929	--------	-0.70109	--------	-0.71199	--------	-0.78170	--------
0.8	-0.99996	-0.43329	--------	-0.42895	--------	-0.45961	--------	-0.45769	--------

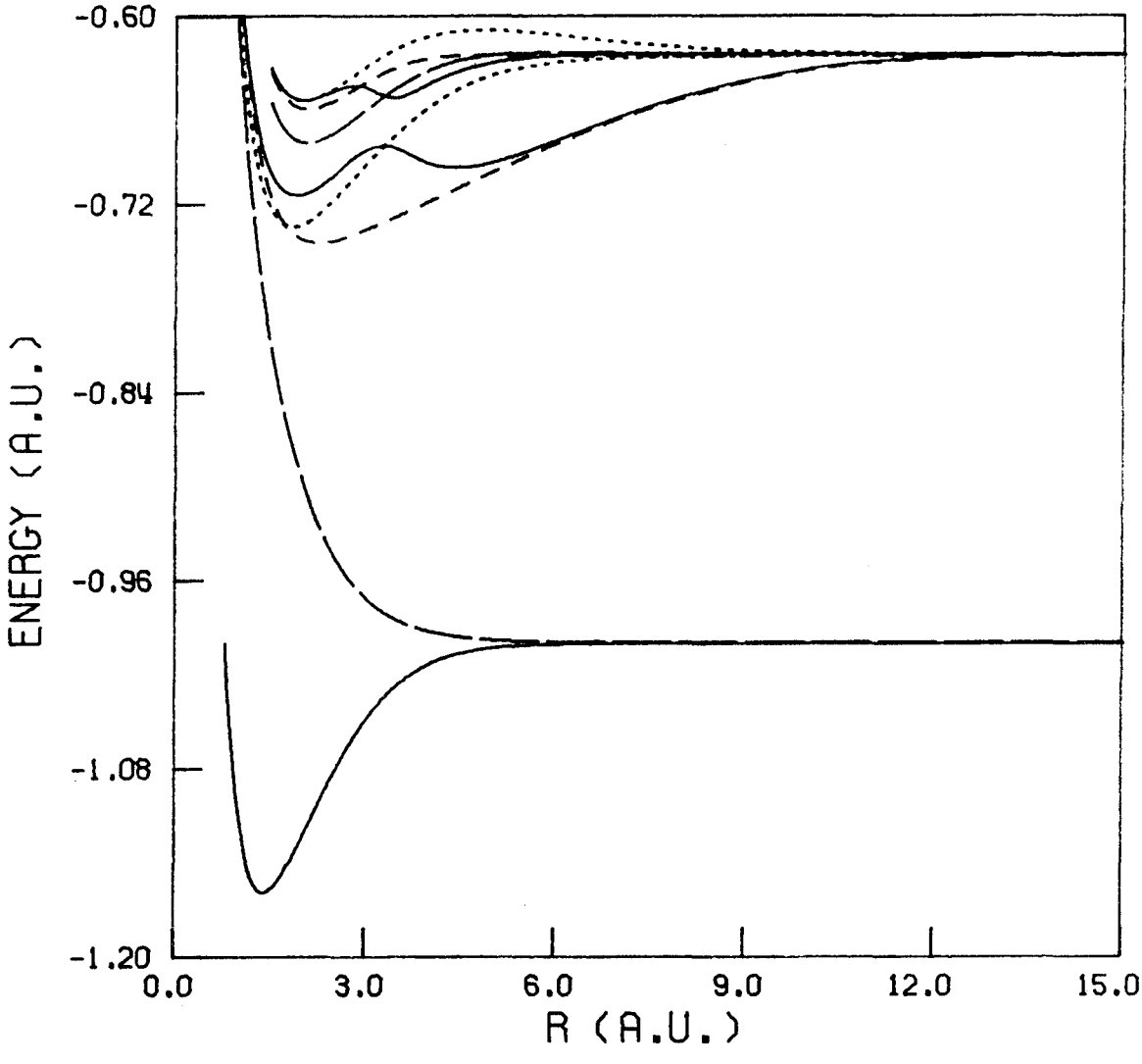


Fig. 2. Ab initio PGVB H_2 total energies (16 basis functions): Solid lines, $^1\Sigma_g^+$; long dashes, $^3\Sigma_u^+$; medium dashes, $^1\Sigma_u^+$; short dashes, $^3\Sigma_g^+$.

TABLE IV. PGVB orbital energies, ϵ_b, for H_2 in the 16 BF basis.

R	$1\,^1\Sigma_g^+$	$2\,^1\Sigma_g^+$	$3\,^1\Sigma_g^+$	$1\,^1\Sigma_u^+$	$2\,^1\Sigma_u^+$	$1\,^3\Sigma_g^+$	$2\,^3\Sigma_g^+$	$1\,^3\Sigma_u^+$	$2\,^3\Sigma_u^+$
∞	-0.49991	-0.12496	-0.12493	-0.12496	-0.12493	-0.12496	-0.12493	-0.49991	-0.12496
16	-0.49996	-0.12497	-0.12473	-0.12527	-0.12495	-0.12521	-0.12492	-0.49996	-0.12492
12	-0.49997	-0.12701	-0.12461	-0.12765	-0.12510	-0.12538	-0.12475	-0.49997	-0.12478
10	-0.49993	-0.13453	-0.12440	-0.13655	-0.12522	-0.12544	-0.12382	-0.49991	-0.12453
8	-0.49974	-0.15453	-0.12396	-0.15735	-0.12534	-0.12564	-0.11948	-0.49925	-0.12398
6	-0.49940	-0.18335	-0.12332	-0.18777	-0.12499	-0.12669	-0.10588	-0.49384	-0.12219
5	-0.50061	-0.19831	-0.12388	-0.20429	-0.12352	-0.12872	-0.09652	-0.48439	-0.11956
4.0	-0.50812	-0.20293	-0.12905	-0.21349	-0.11778	-0.13331	-0.08667	-0.46332	-0.11421
3.5	-0.51751	-0.18619	-0.14182	-0.21180	-0.11115	-0.13687	-------	-0.44540	-0.11037
3.0	-0.53319	-0.14568	-0.14342	-0.20476	-0.10209	-0.14132	-0.07514	-0.42001	-0.10559
2.5	-0.55839	-0.13565	-0.09148	-0.19296	-0.09218	-0.14671	-0.06977	-0.38424	-0.09962
2.0	-0.59763	-0.13769	-0.07349	-0.17862	-0.08250	-0.15312	-0.06495	-0.33606	-0.09357
1.5	-0.65659	-0.14303	-0.06535	-0.16525	-0.07429	-0.16077	-0.06110	-0.27894	-0.09277
1.4	-0.67136	-0.14439	--------	-0.16300	--------	-0.16248	--------	-0.26747	--------
0.8	-0.78637	-0.15462	--------	-0.15273	--------	-0.17427	--------	-0.20906	--------

TABLE V. PGVB H_2 total energies (in a.u.) for the 18 BF basis.

R	$3\,{}^1\Sigma_g^+$	$4\,{}^1\Sigma_g^+$	$2\,{}^1\Sigma_u^+$	$2\,{}^3\Sigma_g^+$	$3\,{}^3\Sigma_g^+$	$2\,{}^3\Sigma_u^+$
2	-0.65853	-0.65272	-0.66203	-0.65884	-0.65802	-0.68127
3	-0.64628	-0.62686	-0.64407	-0.63647	-0.62859	-0.66059
4	-0.64342	-0.60092	-0.62722	-0.61455	-0.59503	-0.63493

The corresponding outer orbital energies, ϵ_b, are given in Table VI.

TABLE VI. PGVB H_2 orbital energies, ϵ_b (in a.u.) for the 18 BF basis.

R	$3\,{}^1\Sigma_g^+$	$4\,{}^1\Sigma_g^+$	$2\,{}^1\Sigma_u^+$	$2\,{}^3\Sigma_g^+$	$3\,{}^3\Sigma_g^+$	$2\,{}^3\Sigma_u^+$
2	-0.07539	-0.06558	-0.08313	-0.07211	-0.06464	-0.09474
3	-0.13891	-0.08211	-0.10129	-0.07874	-0.06351	-0.10558
4	-0.12887	-0.08638	-0.11737	-0.08825	-0.06147	-0.11406

In Fig. 3 we have plots of the φ_a (inner) orbital for several of the states at a few distances. The $1\sigma_g$ orbitals from H_2^+ and the G1 orbital for the H_2 ground state are included for comparison. In each H_2 case, the φ_a orbital resembles a hydrogen 1s orbital on the left. This orbital appears relatively unchanged as we proceed from state to state and does not change much even as R is varied. On the other hand, as shown below, the other orbital (ϕ_b) differs markedly from state to state and in some cases changes significantly as R is varied.

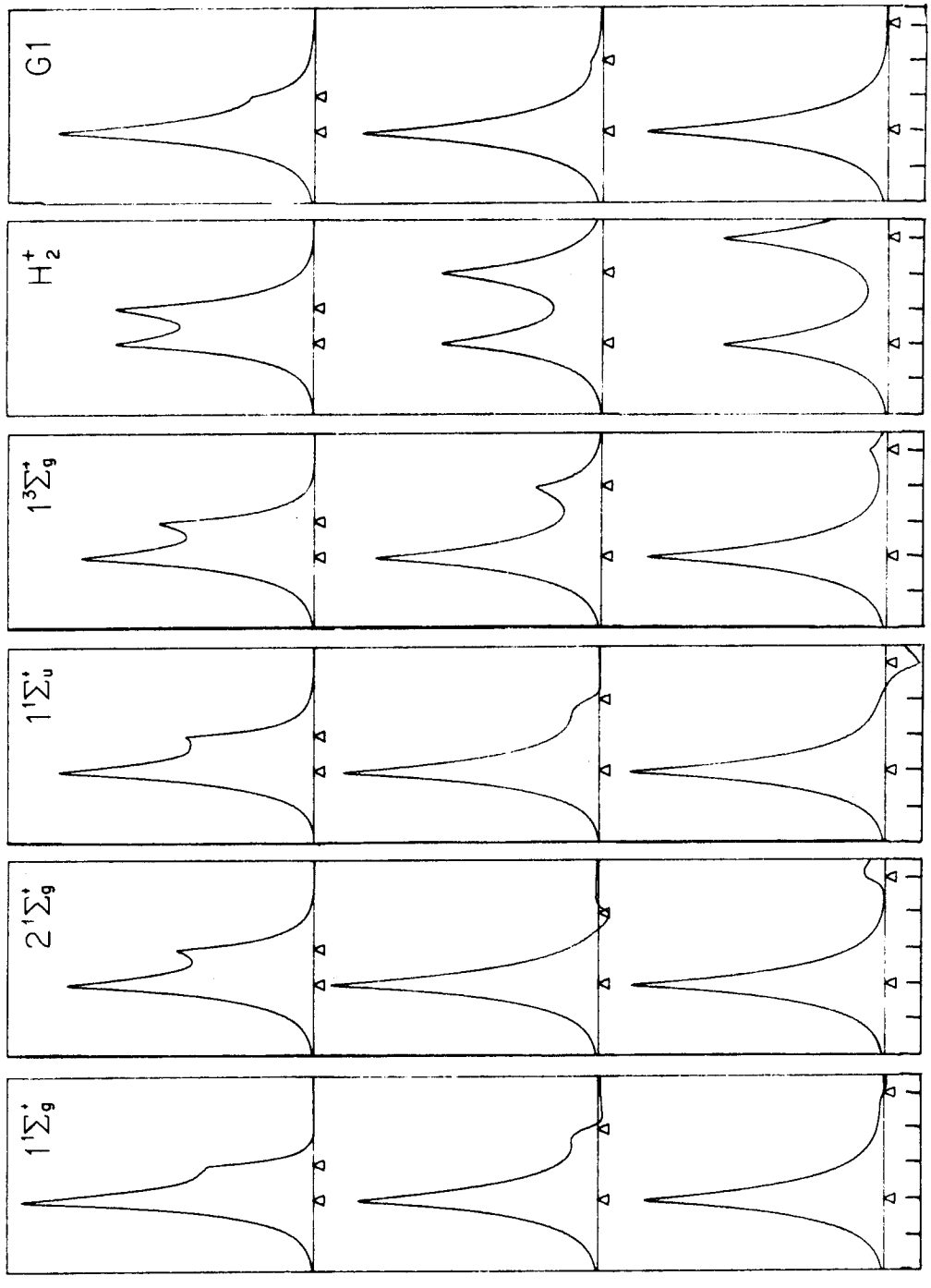


Fig. 3 ϕ_a Orbitals for H_2, PGVB

Thus the various low-lying excited states of H_2 may be described as in (3) where $\phi_a \sim 1s_L$. That is, these states may all be considered as single excitation (of ϕ_b) from a ground state

$$\boxed{\phi_a \phi_b}_g = \boxed{1s_L 1s_R}_g .$$

This suggests that in studying the states of H_2 we may concentrate on the form expected for ϕ_b.

Since ϕ_a is primarily concentrated near the left proton, we would expect ϕ_a to effectively shield the left proton from ϕ_b. Thus the field seen by ϕ_b could be qualitatively viewed as a nearly unshielded proton on the right and a nearly shielded proton on the left (say, an effective charge of $Z_{eff} \sim 1/5$). Then the spectrum of states, $\{\phi_b\}$, and the dependence of each state on R would be expected to resemble that of a one-electron diatomic molecule with charges $Z_L = Z_{eff}$ and $Z_R = 1$. That is, our model for describing the H_2 excited states will be a one-electron heteronuclear diatomic molecule.

C. The One-Electron Model: A few calculations on one-electron diatomics have been reported in the literature.[24-27] A number of observations can be made, summarizing these results, that will be applicable to a description of the states of H_2.

A remarkable aspect of the one-electron two-center problem is the extra symmetry operator[28] (in a. u.)

$$\Omega = L^2 + R^2(\nabla^2 - \frac{\partial^2}{\partial Z^2}) + 2R(Z_1 \cos\Theta_1 - Z_2 \cos\Theta_2) \qquad (60)$$

This extra symmetry is what allows the separation of variables, the crossing of curves otherwise of the same symmetry, and the classification of all the one-electron states by n, ℓ, m quantum numbers just as in atoms.

In Fig. 4 we see line-plots of the wavefunctions for the lowest four σ states of HeH^{+2} (taken from Ref. 25) as functions of the internuclear distance. It is to be noted how smoothly each state varies as R changes. In specific, each state has a characteristic appearance that connects it to the united atom limit for which it is named. In Fig. 5 we have further information about the character of each state, the nodal surfaces for the first eight σ states of HeH^{+2} (from Ref. 27). As Wilson and Gallup[27] have observed, the nodal surfaces are always ellipsoids of revolution,and single sheets of hyperboloids of revolution of two sheets. The resemblance to the nodal surfaces of the corresponding united atom states is pronounced and significant.

In Fig. 6 we have plots of the electronic energies of the lowest eight σ states for HeH^{+2} and LiH^{+3} (from Ref. 27).

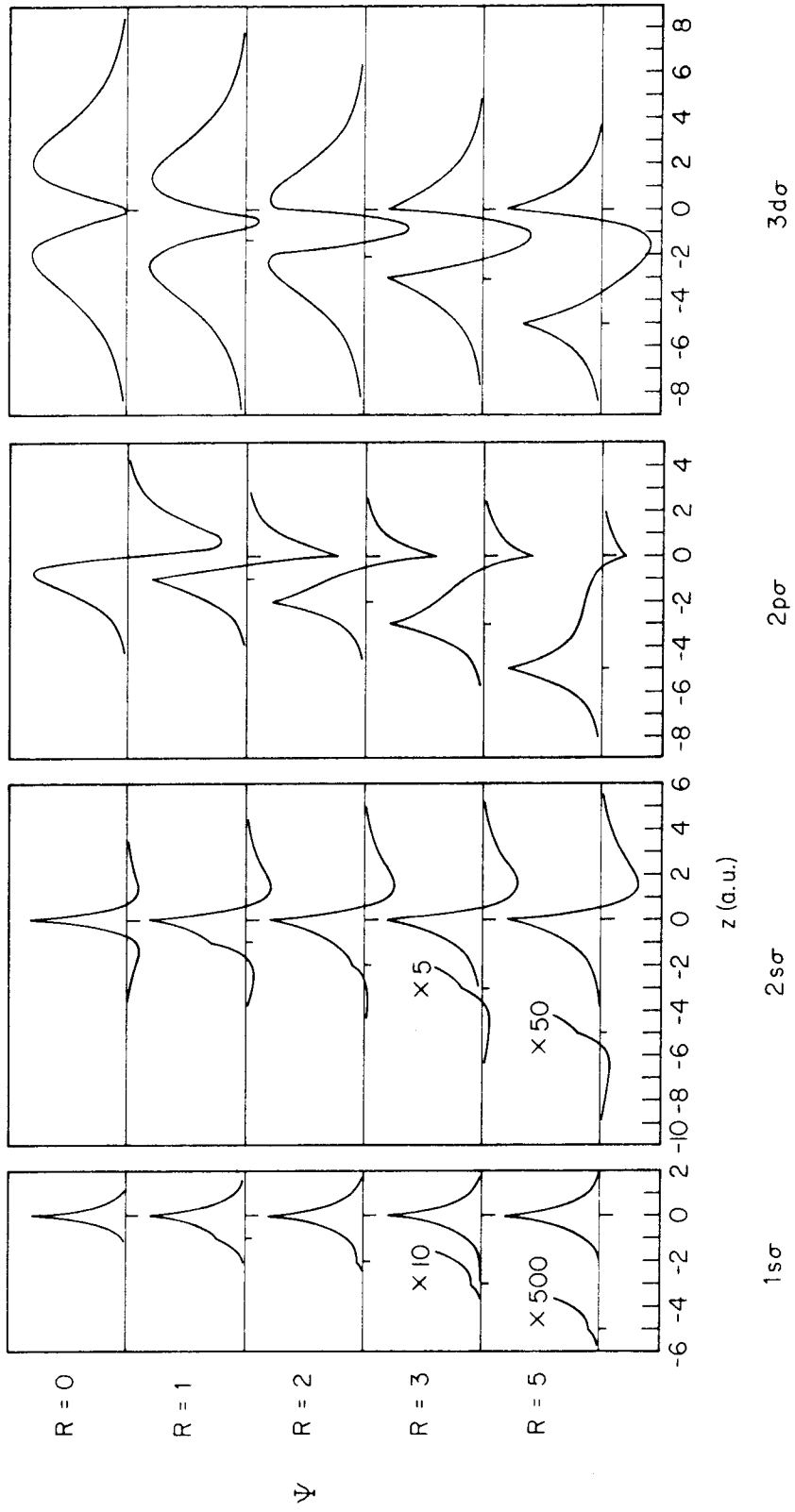


Fig. 4 Exact wave functions of HeH^{+2} [Bates, Carson (1956)]

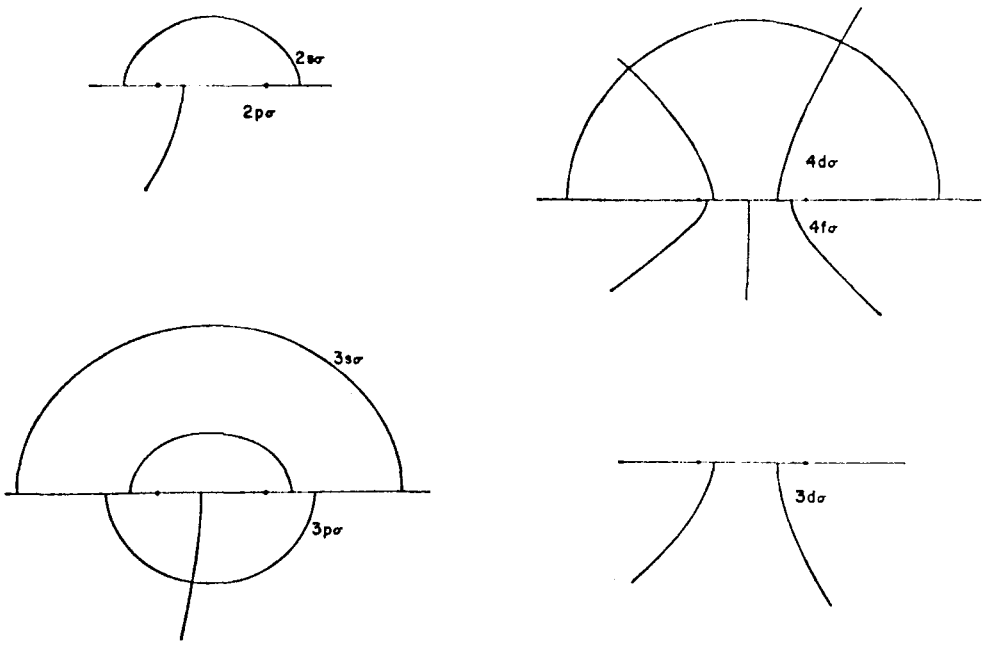


Fig. 5. The nodal surfaces for the first eight σ states of HeH^{+2} at R = 2 a.u., from Ref. 27.

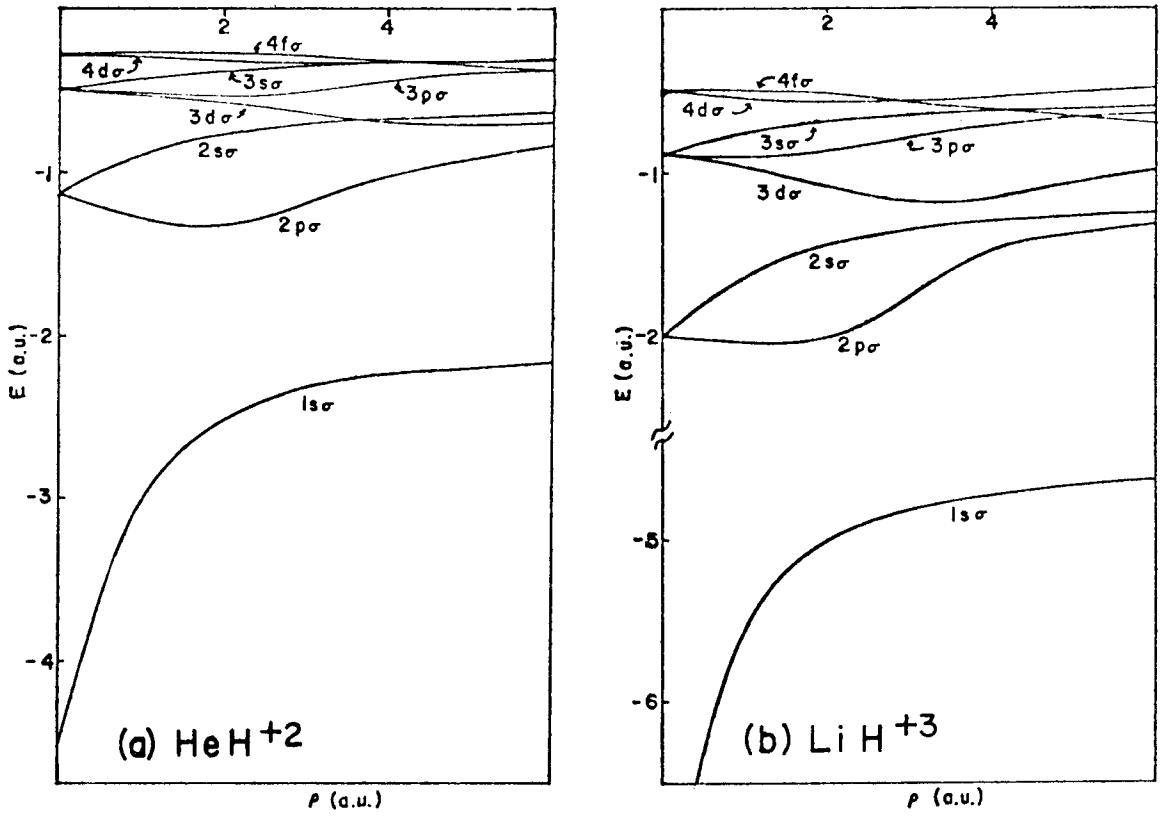


Fig. 6. First eight σ-state electronic energies as functions of the internuclear distance for HeH^{+2} and LiH^{+3}, from Ref. 27.

It is to be noticed that some curves show marked bonding effects, while others are nearly flat. For example, the $1s\sigma$ state, which is a 1s orbital at very large and very small R, contributes strongly to bonding for small R. The $2p\sigma$, $3d\sigma$, $4f\sigma$, etc., states generally lead to bonding and a minimum at large R. This can be understood by noting that the overall size and shape of the various orbitals (i.e., states) of the molecule depend only slightly on the internuclear distance (see Fig. 4), and that each of $n\ell\sigma$ orbitals with $\ell = n - 1$ has two principal concentrations of charge density along the internuclear axis. The minimum energy then occurs for R comparable to the distance between these lobes of charge density. On this basis we expect the maximum bonding (for a total effective charge of 1) in the above $n\ell\sigma$ orbitals (with $\ell = n - 1$) to occur for $R \approx 2n(n - 1)$, i.e., $R \approx 4\,a_0$ for $2p\sigma$, $R \approx 12\,a_0$ for $3d\sigma$, and $R \approx 24\,a_0$ for $4f\sigma$.

An idea associated with this description of bonding is that of ionic character. We consider the system of LiH^{+3}. Crudely speaking, those states that have most of amplitude of the wavefunction near the Li nucleus should have a nearly flat electronic energy curve, dropping only when the centers are quite close (cf. the $2s\sigma$ state above). The electron much prefers to be on the center with the most charge (the Li nucleus). It is relatively uninterested in the smaller center (the proton). But, if the electron should start out on the hydrogen, then its desire to move back to the lithium will cause a rapid drop in the energy as the distance decreases. So states with a large amplitude on both centers (i.e., 2p, 3d, 4f, etc.) will be expected to be binding.

To construct a model for the states of H_2 we need two orbitals, φ_a and φ_b. The effect on the binding due to the outer orbital, φ_b, is to be described as above. The inner or core orbital, φ_a, is basically a 1s orbital as we have seen, slowly becoming an H_2^+ $1\sigma_g$ orbital as R is decreased (see Fig. 3 above). We therefore expect the φ_a orbital to contribute to bonding much as would the $1\sigma_g$ orbital of H_2^+, which is a considerable amount. The total binding is the sum of the contributions of φ_a and φ_b. In Fig. 7 we have the curves obtained by adding the electronic energies from the states of LiH^{+3} (scaled to a total nuclear charge of about 1.3) to the total energy of the ground state of H_2^+. This should give qualitatively accurate energy curves for the various Σ states of H_2.

But we have yet to describe any dependence on spin or spatial symmetry. The H_2 states are to be made (to first order) out of $\varphi_a \simeq 1s_L$, and φ_b from the scaled states of LiH^{+3}. As indicated in Eq. (59), there are four basic couplings of these orbitals and hence four two-electron states resulting from these approximate orbitals (of course, the self-consistent orbitals will not exactly coincide). As shorter and shorter internuclear distances are considered, the wavefunctions for even an asymmetrical system such as LiH^{+3} begin to resemble more closely their united-atom limits. This means, for instance, that the function labeled $2p\sigma$ becomes a 2p atomic function in Be^{+3} (see Fig. 4 for the similar case of $HeH^{+2} \rightarrow Li^{+2}$). In specific, the model state $\varphi_a \varphi_b$ will become 1s2p, the $\underset{\frown}{g}$ component disappearing as $R \rightarrow 0$, leaving only $\underset{\frown}{u}$ symmetry.

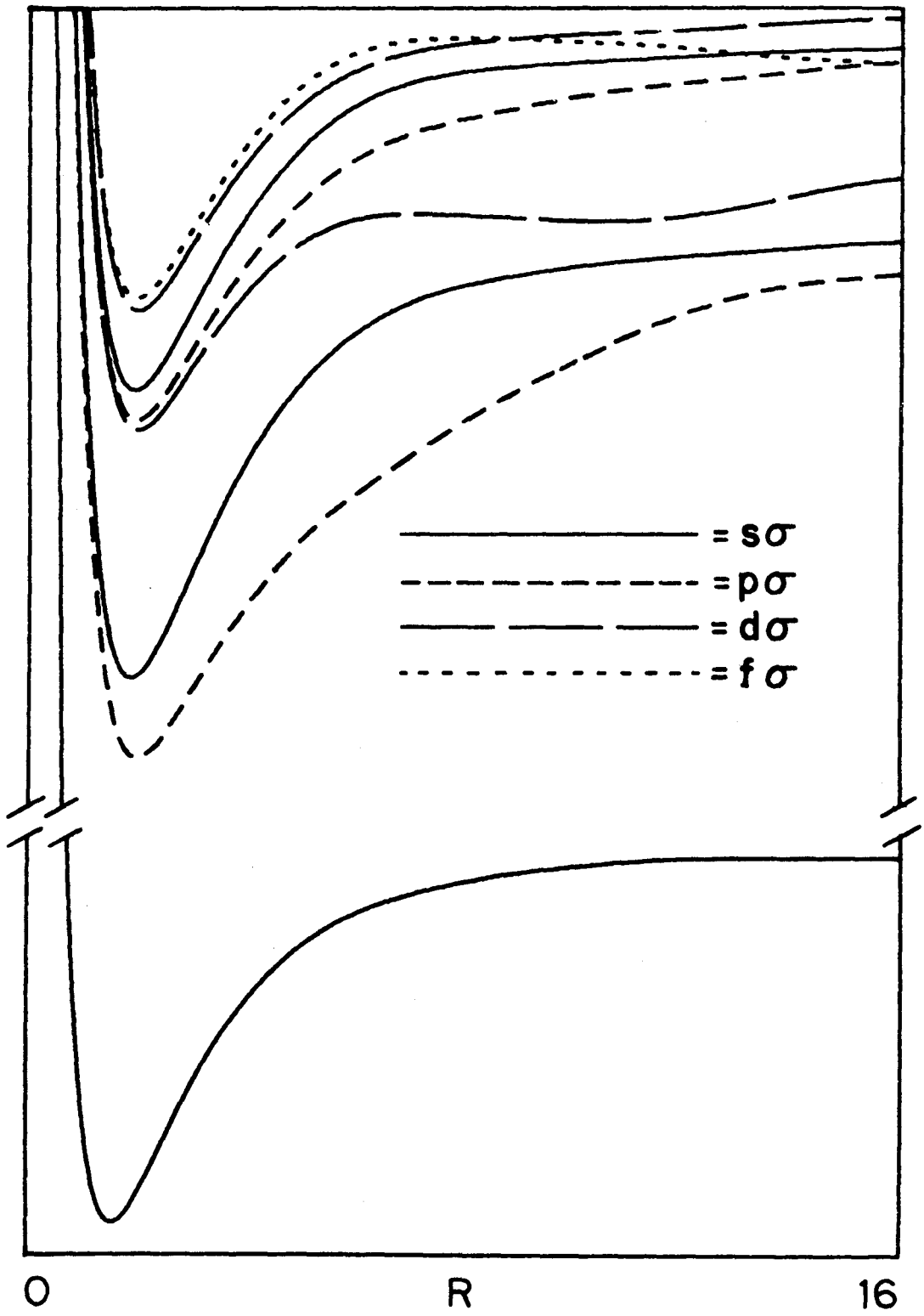


Fig. 7. One-electron model H_2^+ and scaled LiH^{+3}.

At large R the $1s\sigma 2p\sigma$ configuration generates states $^1\Sigma_g^+$, $^1\Sigma_u^+$, $^3\Sigma_g^+$, $^3\Sigma_u^+$ [as in Eq.(59)]. The $^1\Sigma_g^+$ state would be written as $\boxed{1s\sigma 2p\sigma}_g$. If φ_b retains the $2p\sigma$ character all the way to R = 0, then the united-atom wavefunction $\varphi_{1s}\varphi_{2p}$ would have $\underset{\sim}{u}$ spatial symmetry, and the projected wavefunction would vanish. Thus, we know that the self-consistent orbital φ_b must change character before R = 0. For small R, the character of φ_b is expected to be $2s\sigma$, which is the lowest excited state in Fig. 7 that allows $^1\Sigma_g^+$ symmetry for R = 0. The change of character should occur mostly around 3 to $4a_0$; the region in which the n = 2, φ_b orbital begins to overlap significantly with the 1s orbital on the other center (that is, when the wavefunction begins to cancel out).

The $2p\sigma$ orbital is strongly bonding at large R; so the energy of the $2\ ^1\Sigma_g^+$ state should drop rapidly as R is decreased to $\sim 4a_0$. For smaller R the $2p\sigma$ character in φ_b is replaced by $2s\sigma$ character, leading to an increase in energy. Finally, for smaller R (~ 2.5 to $2a_0$), the φ_a orbital contributes to the binding (as in H_2^+) leading to a second energy minimum around $2a_0$ (as in H_2^+). The net result of these effects should be a double minimum in the energy curve for the $2\ ^1\Sigma_g^+$ state as indicated in Fig. 8. This double minimum is well known and will be discussed in greater detail below.

The point of this section is to illustrate how the projection operator may discard a low-energy piece of the wavefunction because it has the wrong united-atom symmetry. The loss of a low-energy component will cause the energy of the state to rise. This will come up repeatedly in the discussion below of the various H_2 states. Indeed, this projected-

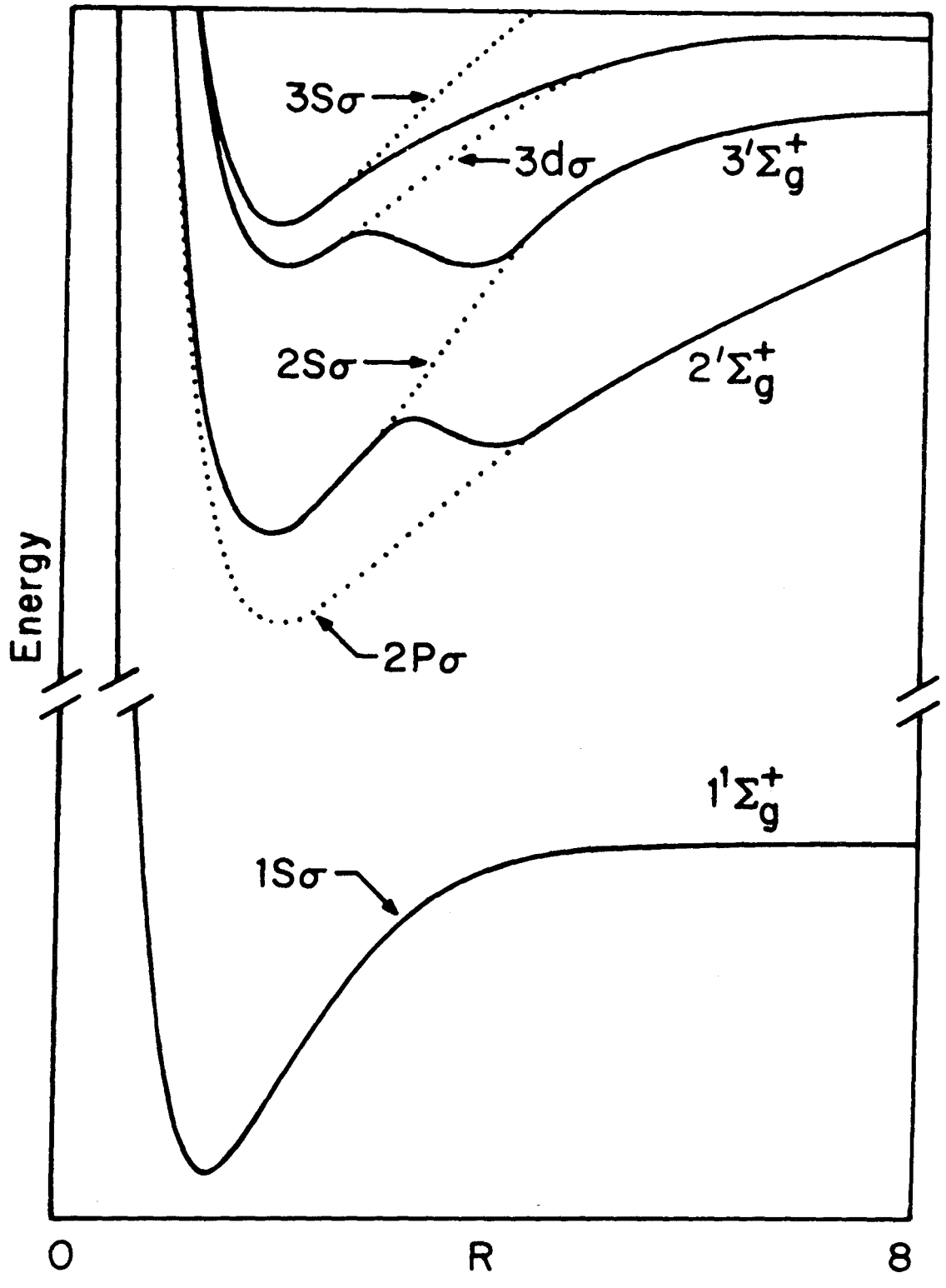


Fig. 8. $^1\Sigma_g^+$ projected correlation diagram.

out component may be handed from state to state as it rises and crosses each state in turn as R decreases. We might call it a diabatic state. This may explain the observed predissociation in the $^1\Sigma_g$ H_2 states[29] and dissociative recombination in He_2.[30]

D. The States of H_2: In this section we will consider individually the various low-lying Σ states of H_2. Of particular concern will be the classification of the states according to orbital character, manifested in the shapes of the orbitals and potential curves. Comparison with previous theoretical and experimental work will be made.

The $^1\Sigma_g^+$ States:

The ground state of H_2, designated X $^1\Sigma_g^+$ or 1 $^1\Sigma_g^+$, probably has received more attention from theorists than any other molecular state. The outer orbital, φ_b, as shown in line-plots in Fig. 9, begins as a hydrogen 1s at large R on the right hand proton and continuously tends toward the 1s′ outer orbital of the ground state of the helium atom. The X state is characterized by the configuration $\boxed{1s\sigma_L 1s\sigma_R'}_g$. The PGI energy curve is shown in Fig. 10 along with the G1 curve (from Ref. 31) and the essentially exact result of Kolos and Wolniewicz.[32]

The first excited $^1\Sigma_g^+$ state (called E and F) shows a remarkable double minimum in its potential curve (as has been mentioned before). The change in orbital character of φ_b from $2p\sigma$ to $2s\sigma$ is clearly shown in the line-plots (Fig. 11), and contour plots (Fig. 12a). Compare, in specific, the line-plots at R = 8 and R = 1 with the HeH^{+2} plots (Fig. 4) $2p\sigma$ at R = 5 and $2s\sigma$ at R = 1. The potential curves are shown in Fig.

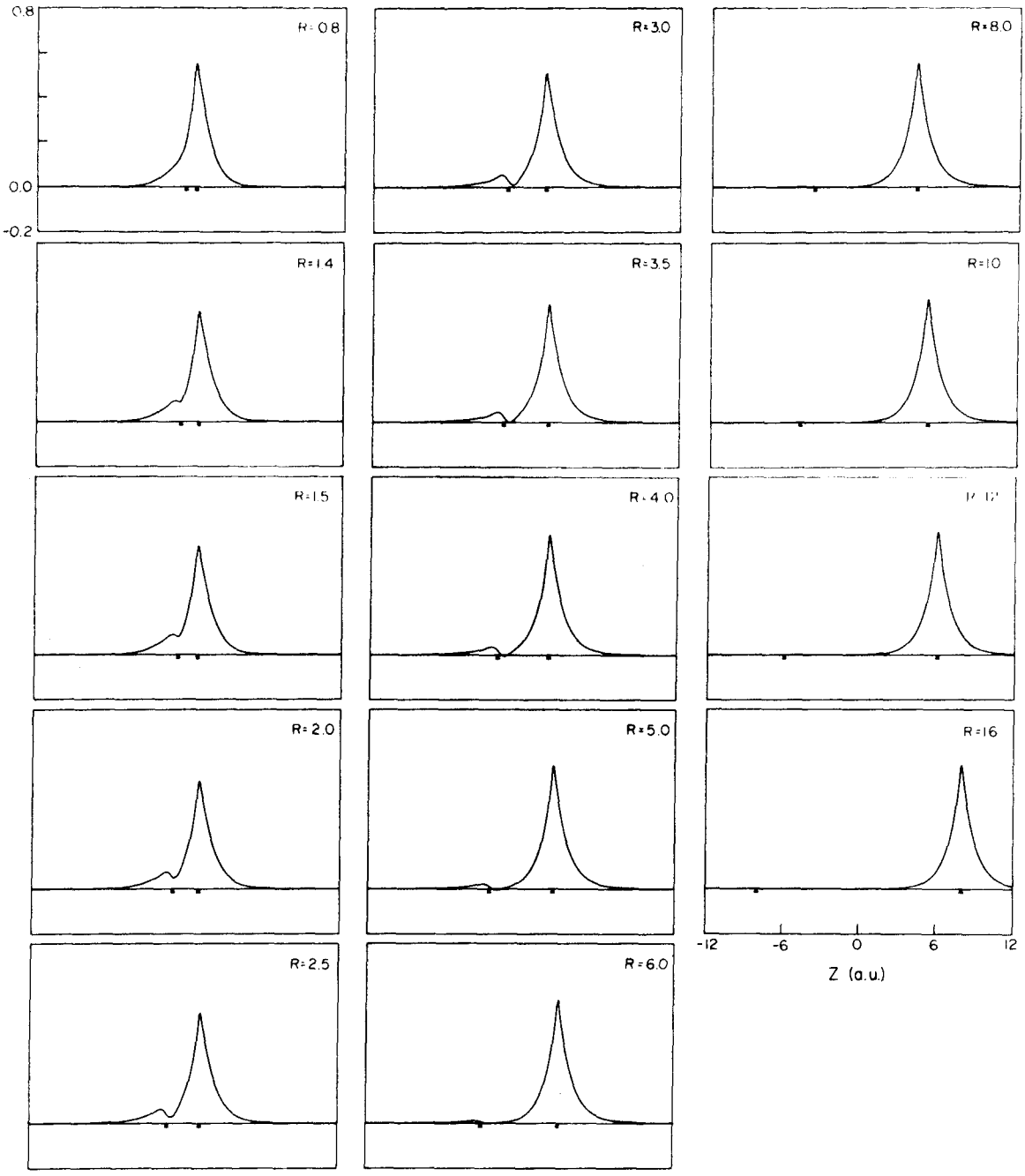


Fig. 9. φ_b orbitals for the $1\ ^1\Sigma_g^+$ state of H_2, PGVB.

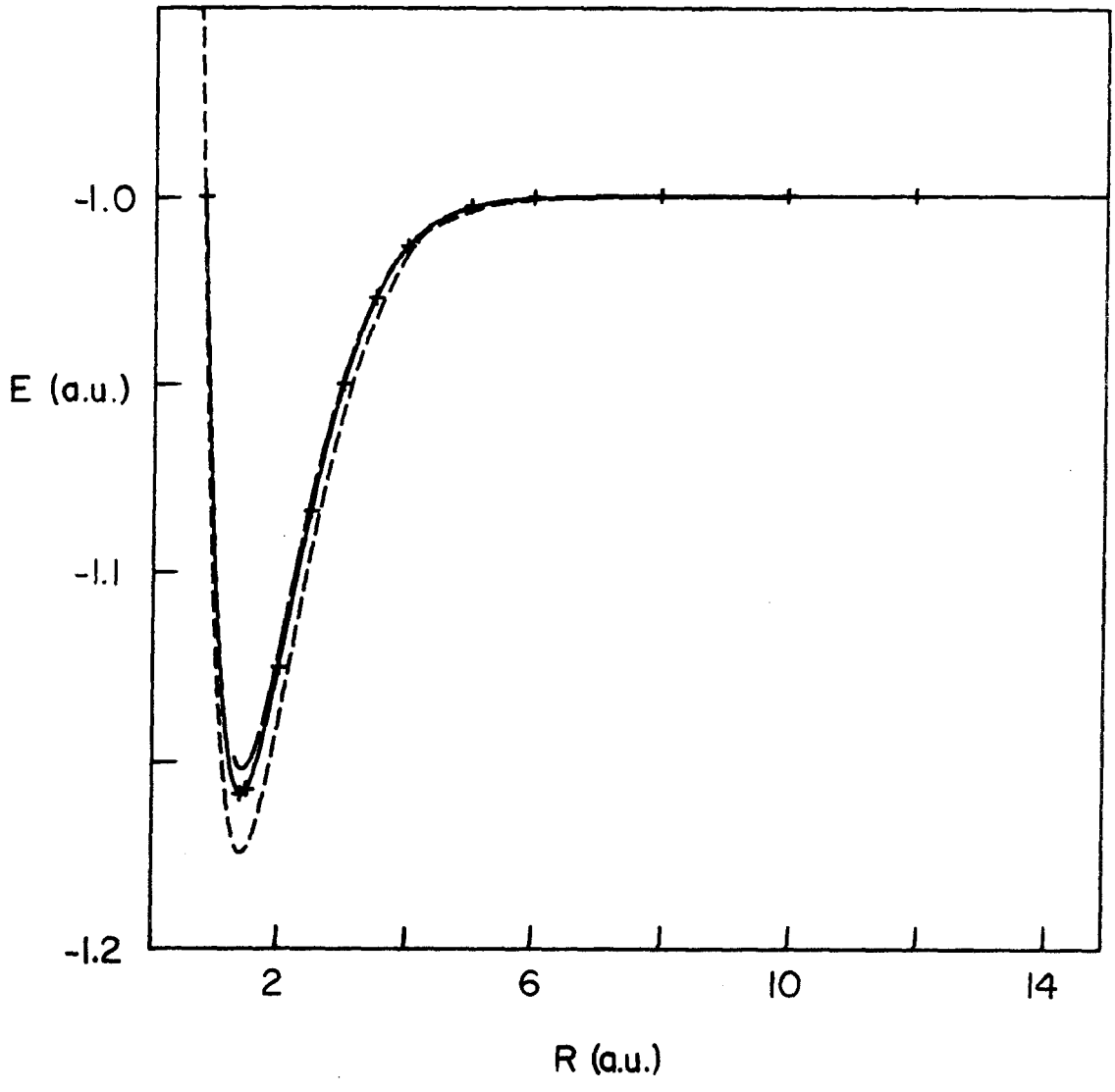


Fig. 10. Total energies for the $1\ ^1\Sigma_g^+$ state of H_2 (called X): long dashes, G1 (Ref. 31); medium dashes, exact (Ref. 32); solid line and crosses, present calculation (16 basis functions).

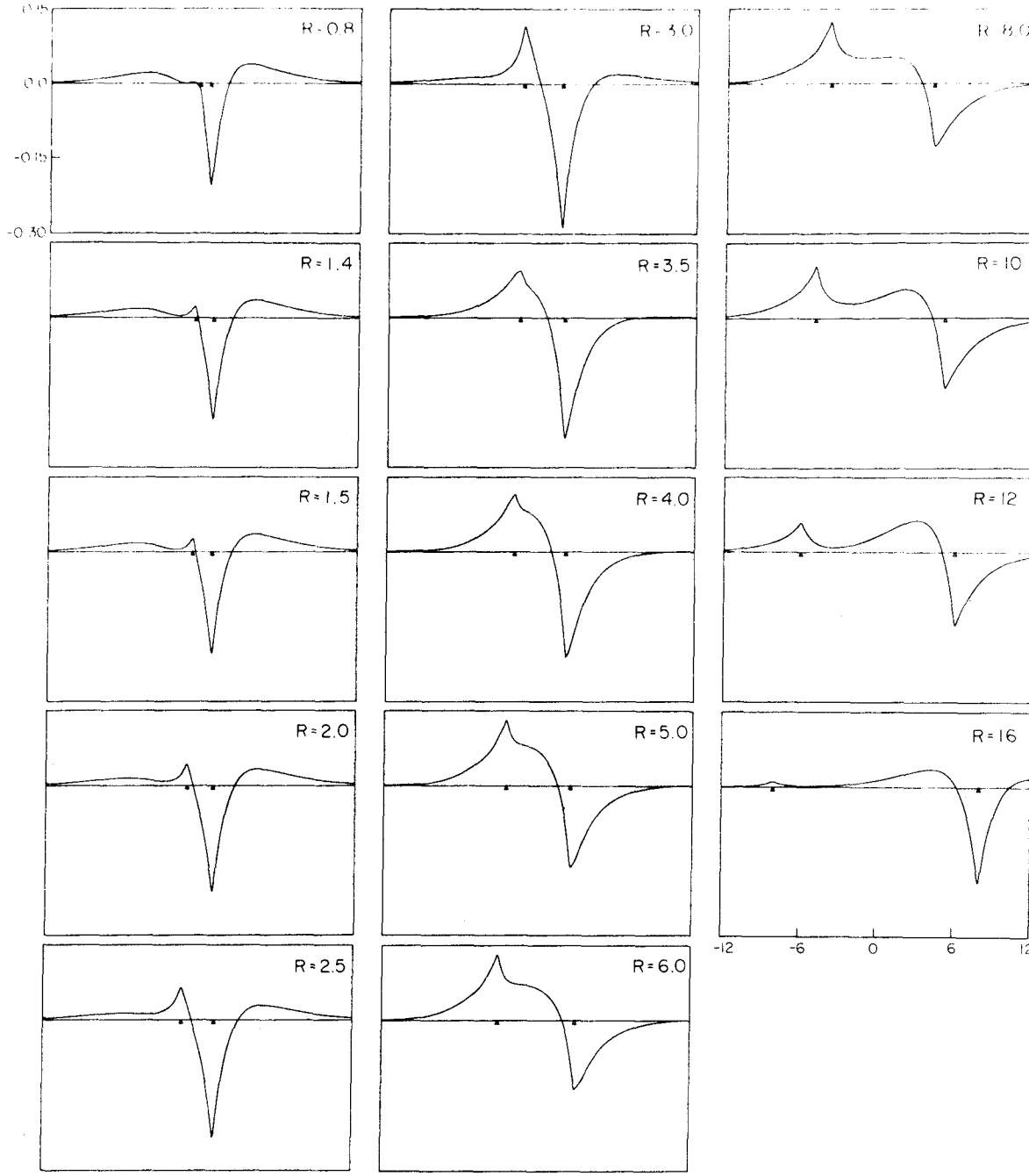


Fig. 11. φ_b orbitals for the 2 $^1\Sigma_g^+$ state of H_2, PGVB (16 basis functions).

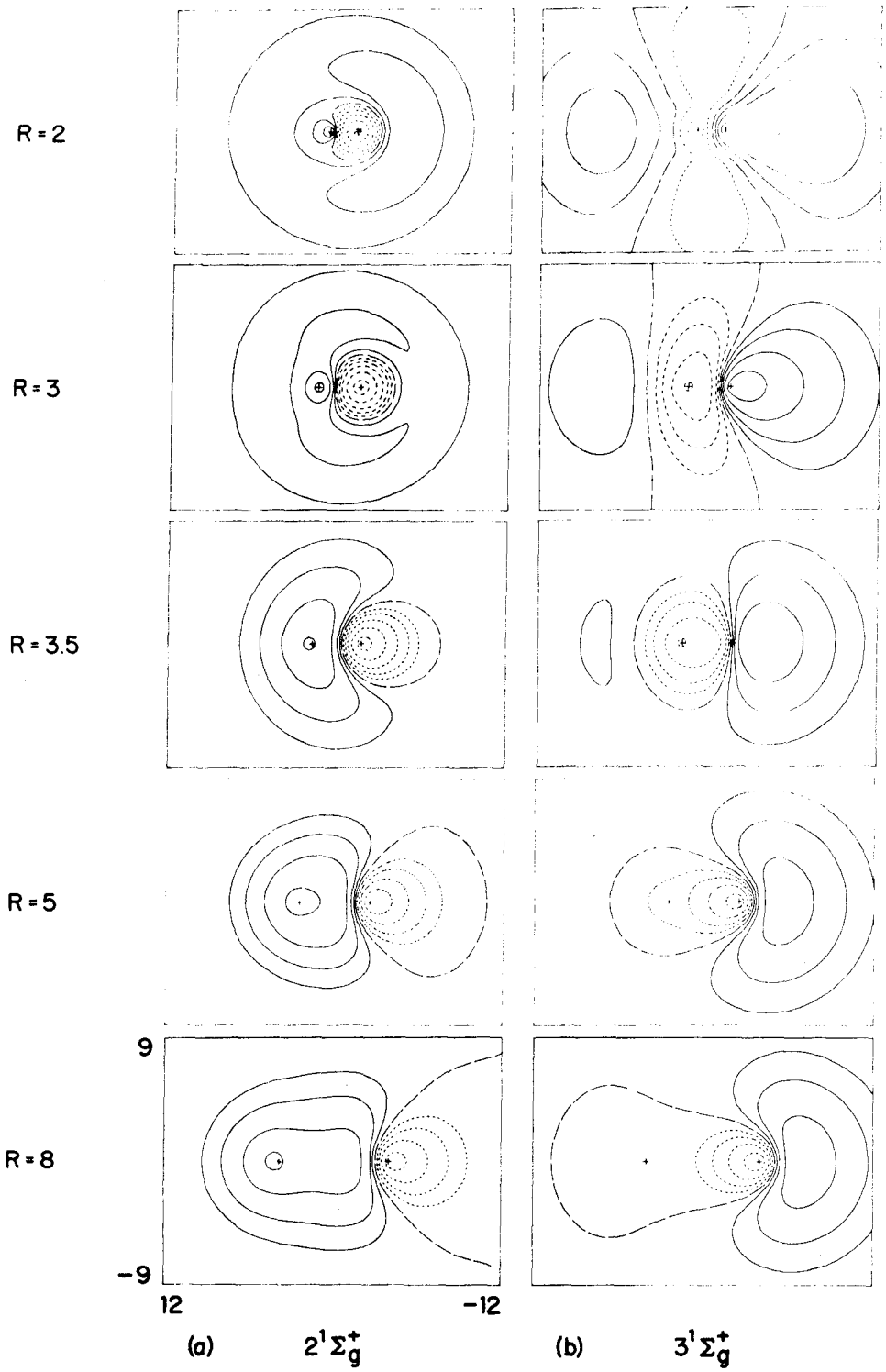


Fig. 12. φ_b orbitals for H_2, PGVB (16 basis functions) contours 0, ± 0.01, ± 0.02, ± 0.04, ± 0.08.

13. The present (16 basis function) calculation is compared with the more complete 32-configuration wavefunction of Davidson[33] (the discoverer of the double minimum), and once again the essentially exact result of Kolos and Wolniewicz.[34]

Examination of the line-plots (Fig. 11) for R = 12 to about R = 3.5 shows a considerable amplitude on the proton that already has a 1s electron. To this sharing of the outer electron, ionic character if you will, we may attribute the strong binding shown in the R = 4 to R = 12 region. The orbital is $2p\sigma$-like, the lowest orbital with much amplitude on both centers. An interesting manifestation of this large ionic component is the large error between the present projected orbital product energy and the exact energy of Ref. 34 near the outer minimum. A negative ion state, such as H^-, is relatively poorly described without angular correlation. The outer electron is weakly bound anyway so correlation is a large effect. The wavefunction of Kolos and Wolniewicz[34] has a complete description of the angular correlation (π^2, δ^2, etc., terms). The present simple orbital product has no angular correlation terms at all.

The standard MO treatment describes the outer minimum as being due to the doubly excited configuration $(1\sigma_u)^2$. This is accurate only to the extent that it illustrates that the σ_u components of the two orbitals play a significant role. But as Figs. 11 and 12a abundantly show, the φ_b orbital retains the diffuseness of a 2s or 2p hydrogenic function at all internuclear distances; the φ_a orbital is always 1s-like in extent (as shown in Fig. 3); and we therefore conclude that the contribution of

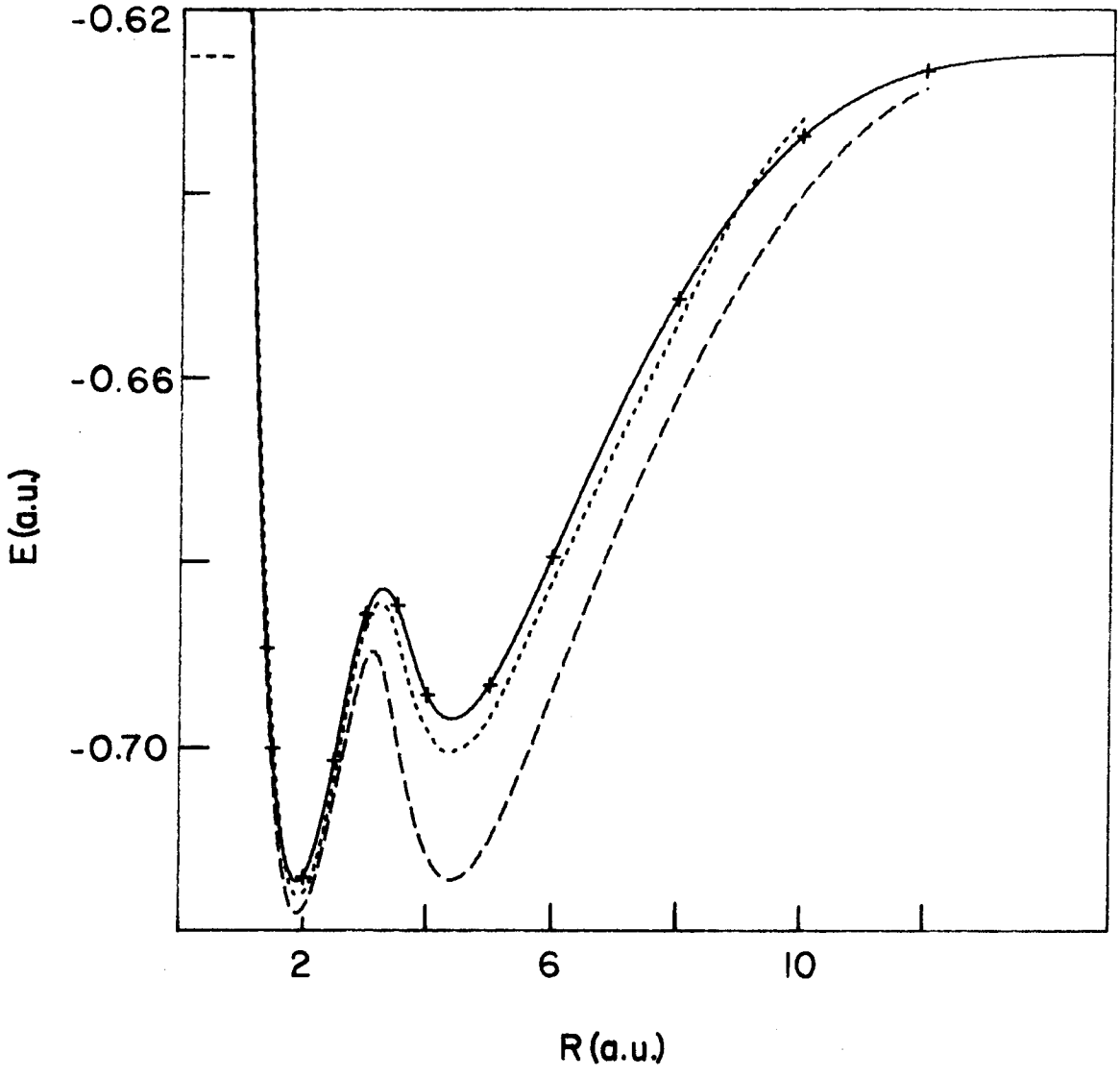


Fig. 13. Total energies for the 2 $^1\Sigma_g^+$ state of H_2 (called E-F): short dashes, CI (Ref. 33); medium dashes, exact (Ref. 34); solid line and crosses, present calculation (16 basis functions).

the $(1\sigma_u)^2$ configuration is mainly heuristic.

Less is known about the third $^1\Sigma_g^+$ state. The state should correlate with the 2s ± 2p level of H and the 3s state of He at the separated- and united-atom limits, respectively. This state has therefore been attributed 3s character and has been named H.[35] Looking at Fig. 8, we see that indeed 2sσ character is expected at large R, that the state should have a double minimum as the 2 $^1\Sigma_g^+$ state steals the 2sσ character, and that for small R the state should be 3dσ-like. The 3sσ state is the next higher (see also below).

The line-plots (Fig. 14) and contour plots (Fig. 12b) show that indeed this is what happens. The corresponding plots with the larger basis are given in Fig. 15. Finally, the energies are given in Fig. 16. The results of Davidson[33b] (of mediocre quality) and Rothenberg and Davidson[36] (of high quality) are shown for comparison. That the 3 $^1\Sigma_g^+$ state was in fact of 3dσ character near R = 2 rather than 3sσ seems to have been first noticed by Wakefield and Davidson.[37] Unravelling the experimental spectrum for this state still awaits further effort.

Even worse off is the 4 $^1\Sigma_g^+$ state (called G). Figures 7 and 8 predict it to be of 3sσ character near R = 2, of 3dσ character for large R, and to have a broad minimum around R = 12. The 18 basis function projected φ_b orbitals are shown in Fig. 17, the energies along with those of Refs. 33b and 36 in Fig. 18.

Finally the excited $^1\Sigma_g^+$ states are summarized by a plot of their orbital energies in Fig. 19. We can in fact see the evidence of the changing of orbitals. The curves rise and fall, nearly crossing as

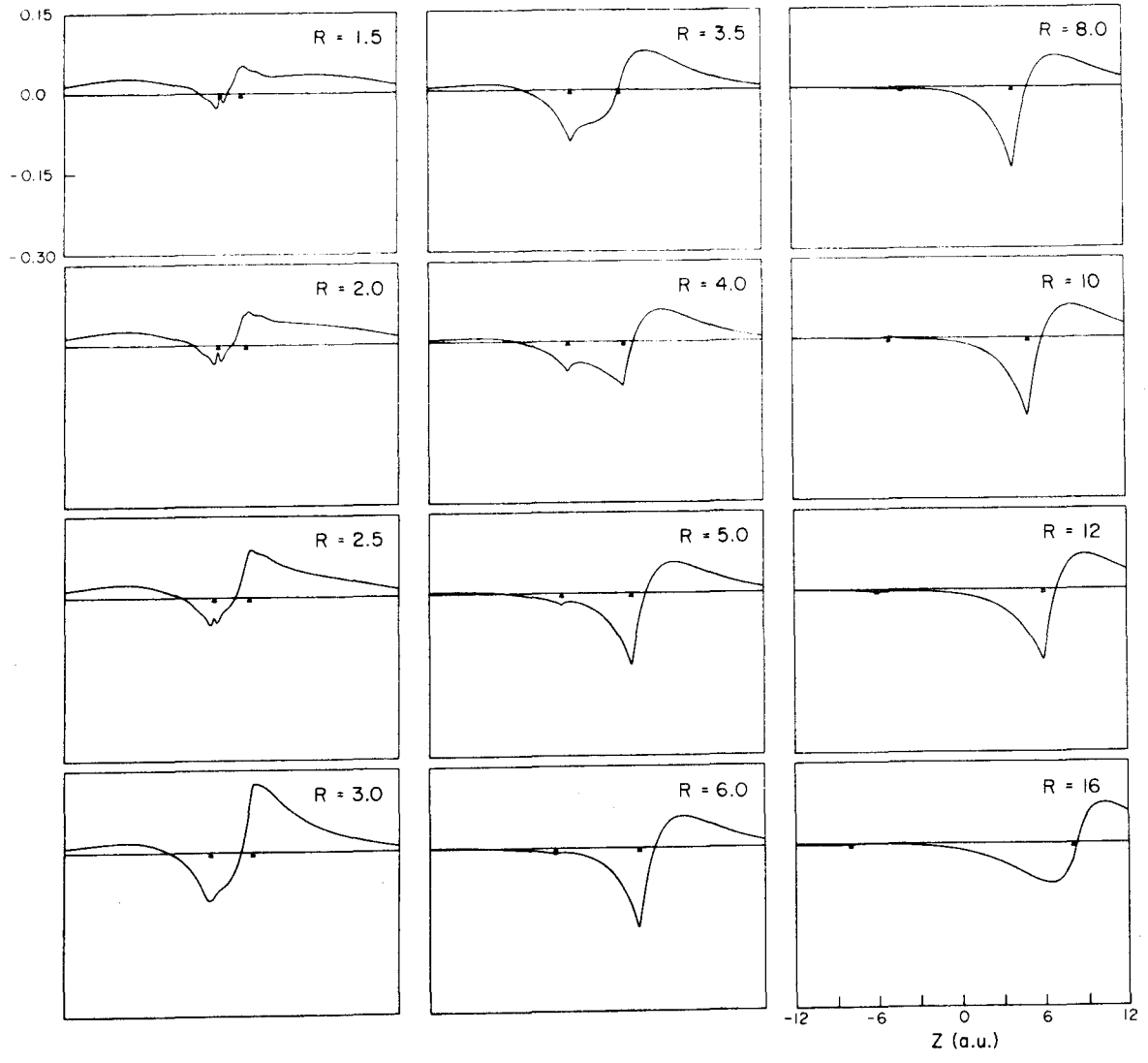


Fig. 14. φ_b orbitals for the $3\ ^1\Sigma_g^+$ state of H_2, PGVB (16 basis functions).

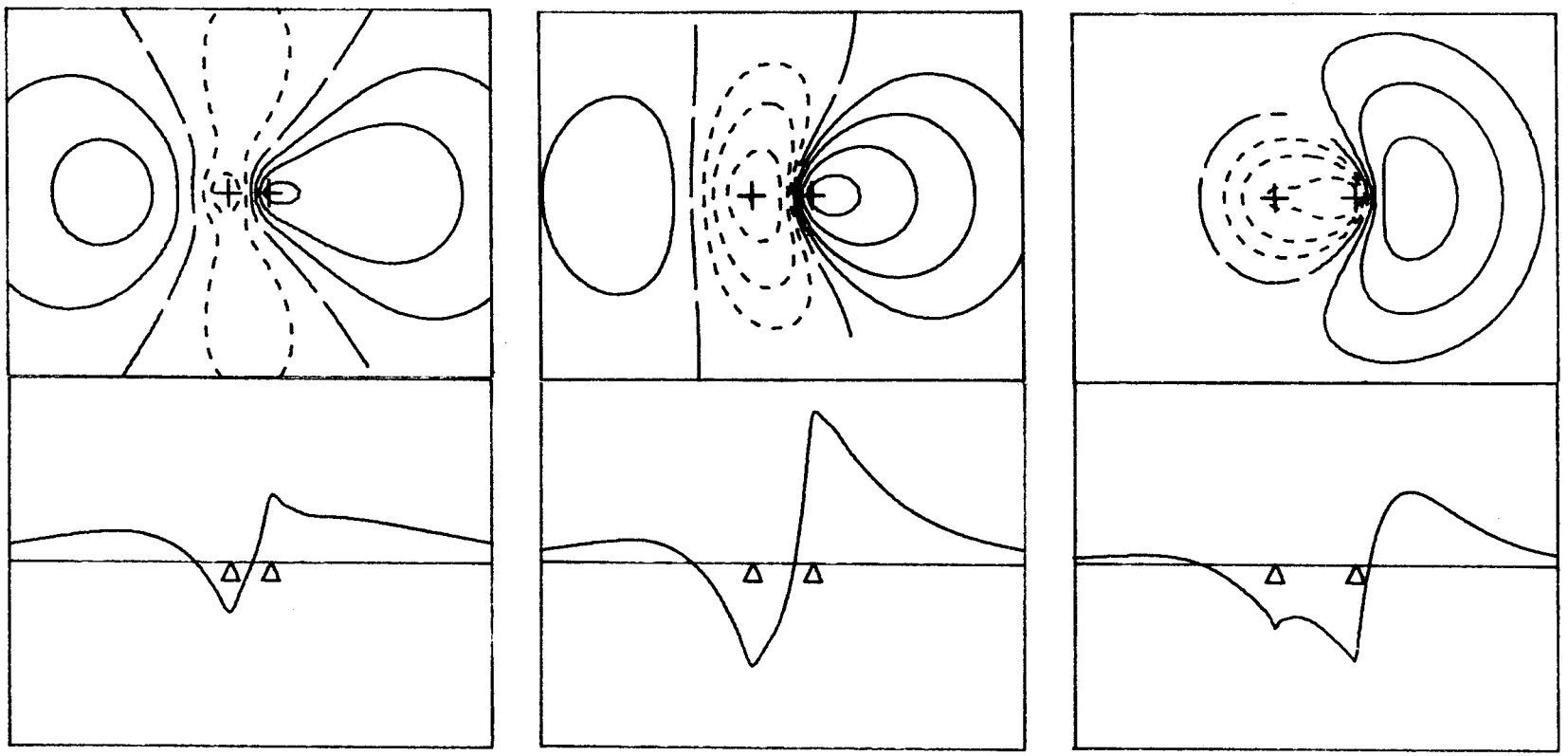


Fig. 15. φ_b orbitals for the 3 $^1\Sigma_g^+$ state of H_2; PGVB (18 basis functions); from left to right R = 2, 3, 4; horizontal scale ± 12 a.u.; vertical scale contour plot ± 9 a.u.; line plot ± 0.15 amplitude; contours 0, ± 0.01, ± 0.02, ± 0.04, ± 0.08.

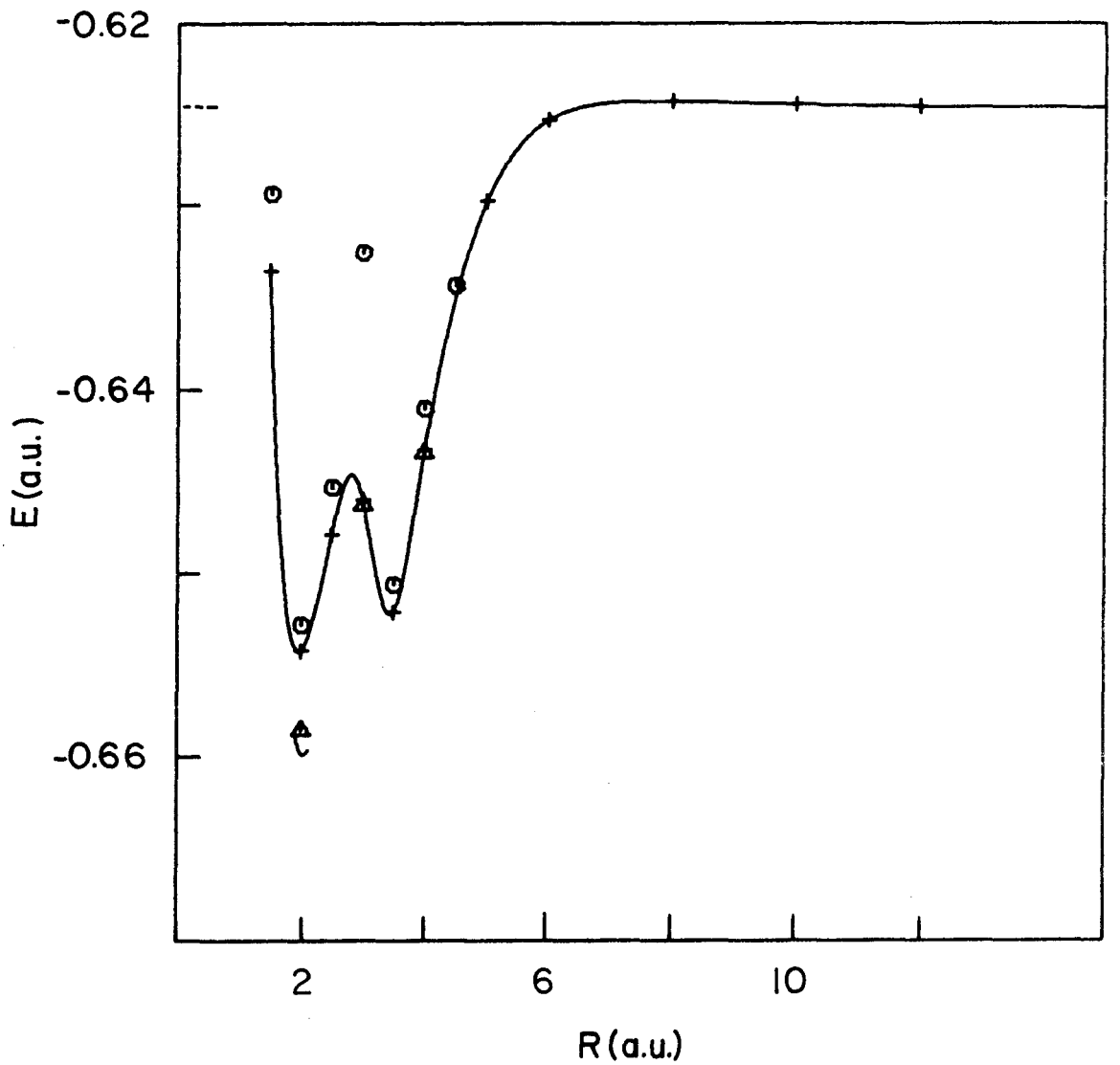


Fig. 16. Total energies for the $3\ ^1\Sigma_g^+$ state of H_2 (called H): circles, CI (Ref. 33b); short solid arc from R = 1.9 to R = 2.1, CI (Ref. 36); solid line and crosses, present calculation (16 basis functions); triangles, present calculation (18 basis functions).

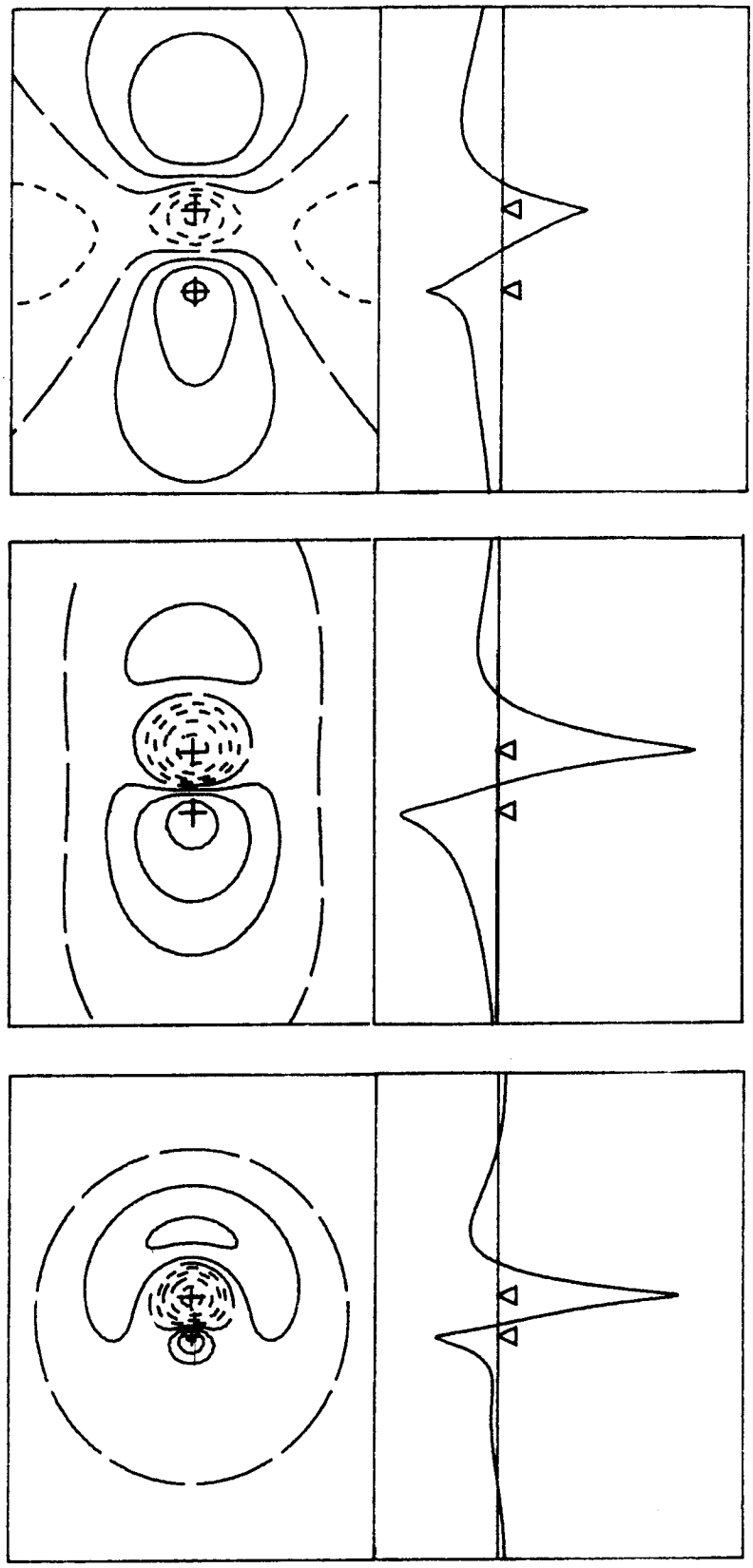


Fig. 17. φ_b orbitals for the 4 $^1\Sigma_g^+$ state of H_2; PGVB (18 basis functions); from left to right R = 2, 3, 4; horizontal scale ± 12 a.u.; vertical scale contour plot ± 9 a.u.; line plot - 0.20 to + 0.10 amplitude; contours 0, $\pm$ 0.02, $\pm$ 0.04, $\pm$ 0.08.

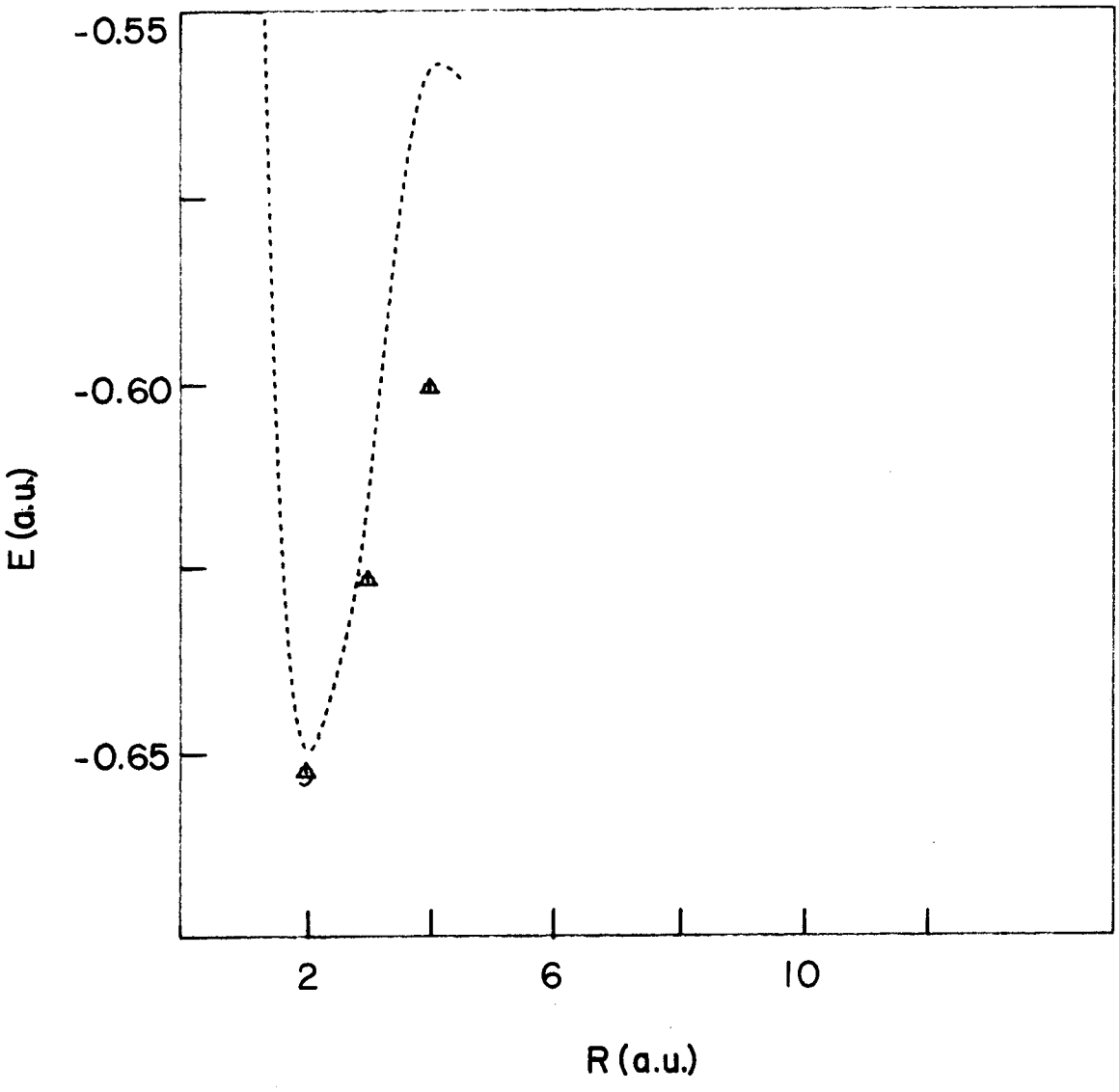


Fig. 18. Total energies for the 4 $^1\Sigma_g^+$ state of H_2 (called G): short dashes, CI (Ref. 33b); short solid arc from R = 1.9 to R = 2.1, CI (Ref. 36); triangles, present calculation (18 basis functions).

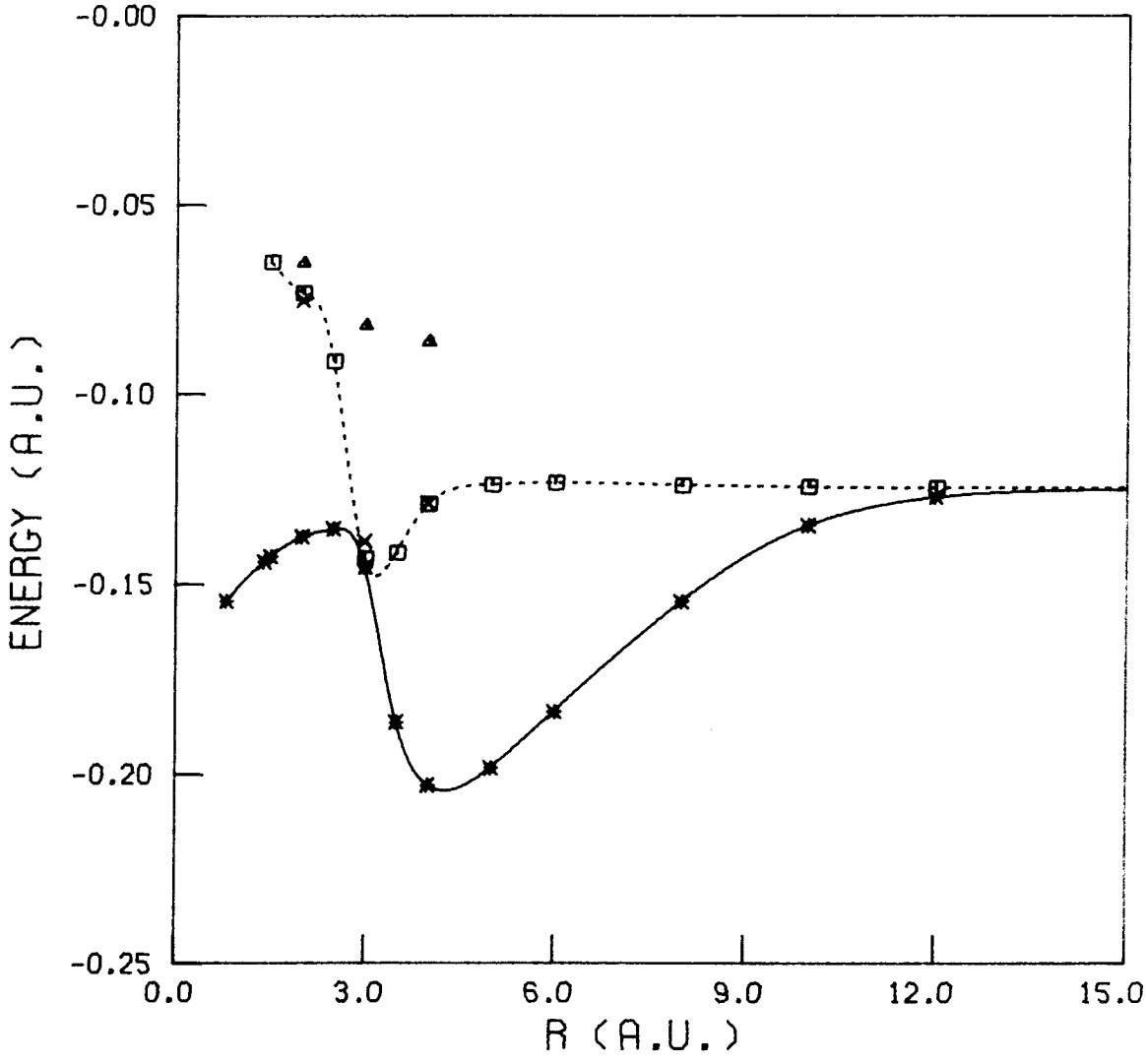


Fig. 19. PGVB orbital energies, ϵ_b, for excited $^1\Sigma_g^+$ states of H_2: solid line and asterisks, 2 $^1\Sigma_g^+$ (16 basis functions); short dashes and squares, 3 $^1\Sigma_g^+$ (16 basis functions); X's, 3 $^1\Sigma_g^+$ (18 basis functions); triangles, 4 $^1\Sigma_g^+$ (18 basis functions).

they exchange orbitals. The $2p\sigma$ character will disappear off the top of the page after crossing every $^1\Sigma_g^+$ state.

The $^1\Sigma_u^+$ States:

The first or B $^1\Sigma_u^+$ state is famous for its broad potential minimum. The outer orbital is of $2p\sigma$ character for all internuclear distances, as illustrated in Figs. 20 and 21a. The broad minimum is due to the strong binding nature of the $2p\sigma$ orbital (as discussed above). The potential curves are shown in Fig. 22. Comparison curves from previous calculations[38-40] are also shown.

The MO description of this state is $1\sigma_g 1\sigma_u$, but once again the plots of the φ_b orbital indicate no variation from the diffuse 2p character.. This is the prototype "V" valence excited state. Once again the MO description merely is a guide rather than a characterization. The state is as diffuse as a 2p Rydberg state at all distances. Indeed the error between the projected curve and the exact curve in Fig. 22 shows that angular correlation will play a large role, and that the wavefunction will tighten up, but not enough to make it a "valence" state.

Interest has developed in the 2 $^1\Sigma_u^+$ state (called B′) concerning whether its curve crosses that of the D $^1\Pi_u$ state.[41] This state begins as $2s\sigma$ at large R and becomes $3p\sigma$ at small R as the $2s\sigma$ character is destroyed by the projection operator, as shown in Figs. 23 and 21b. My potential curve in Fig. 24 shows a very shallow minimum at large R, a hump around R = 5 and a deeper minimum at R = 2. Such a hump is missing in the RKR experimental curve also shown. Perhaps

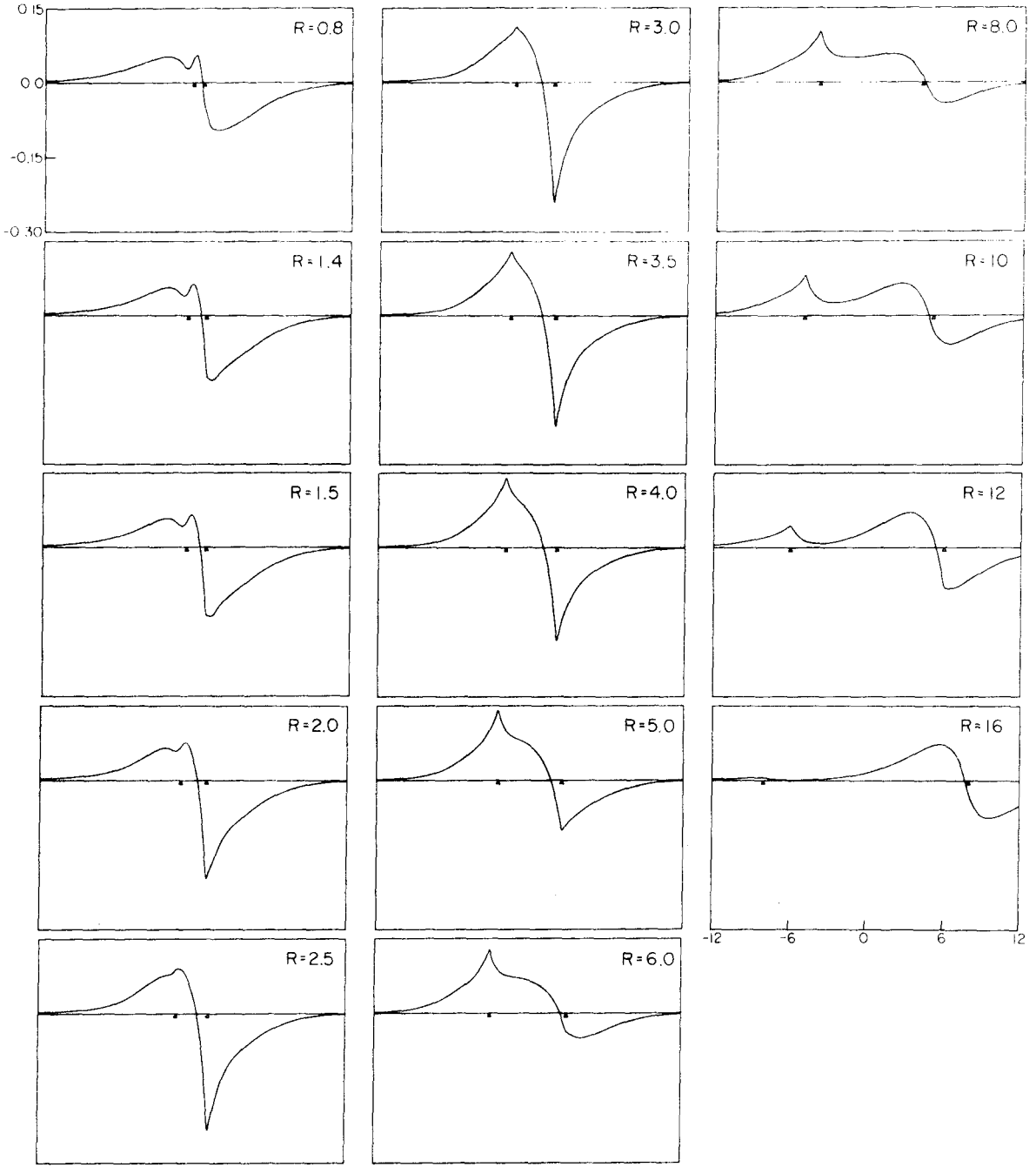
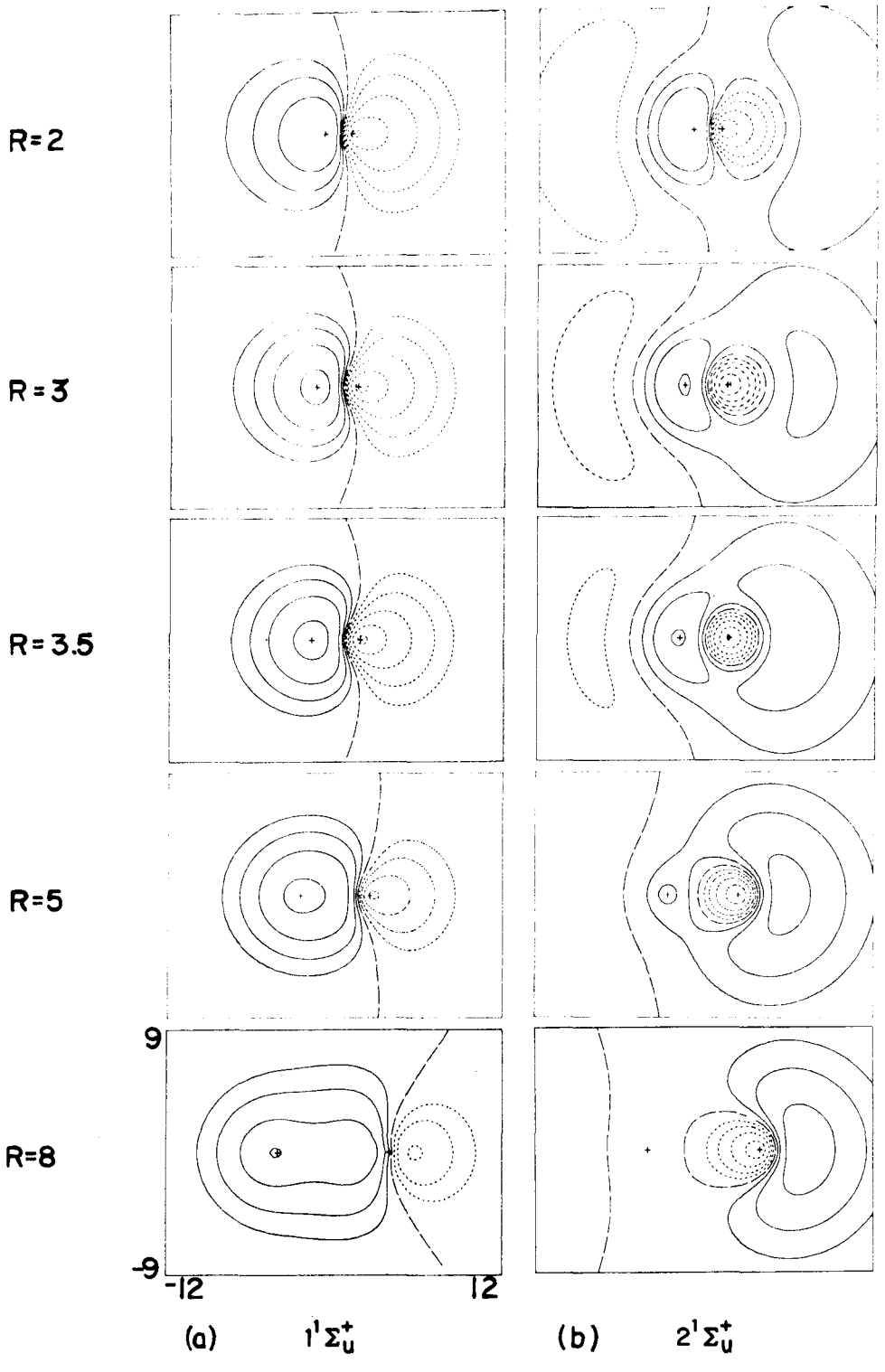


Fig. 20. φ_b orbitals for the $1\ ^1\Sigma_u^+$ state of H_2, PGVB (16 basis functions).



Ref. 21. φ_b orbitals for H_2, PGVB (16 basis functions) contours 0, ± 0.01, ± 0.02, ± 0.04, ± 0.08.

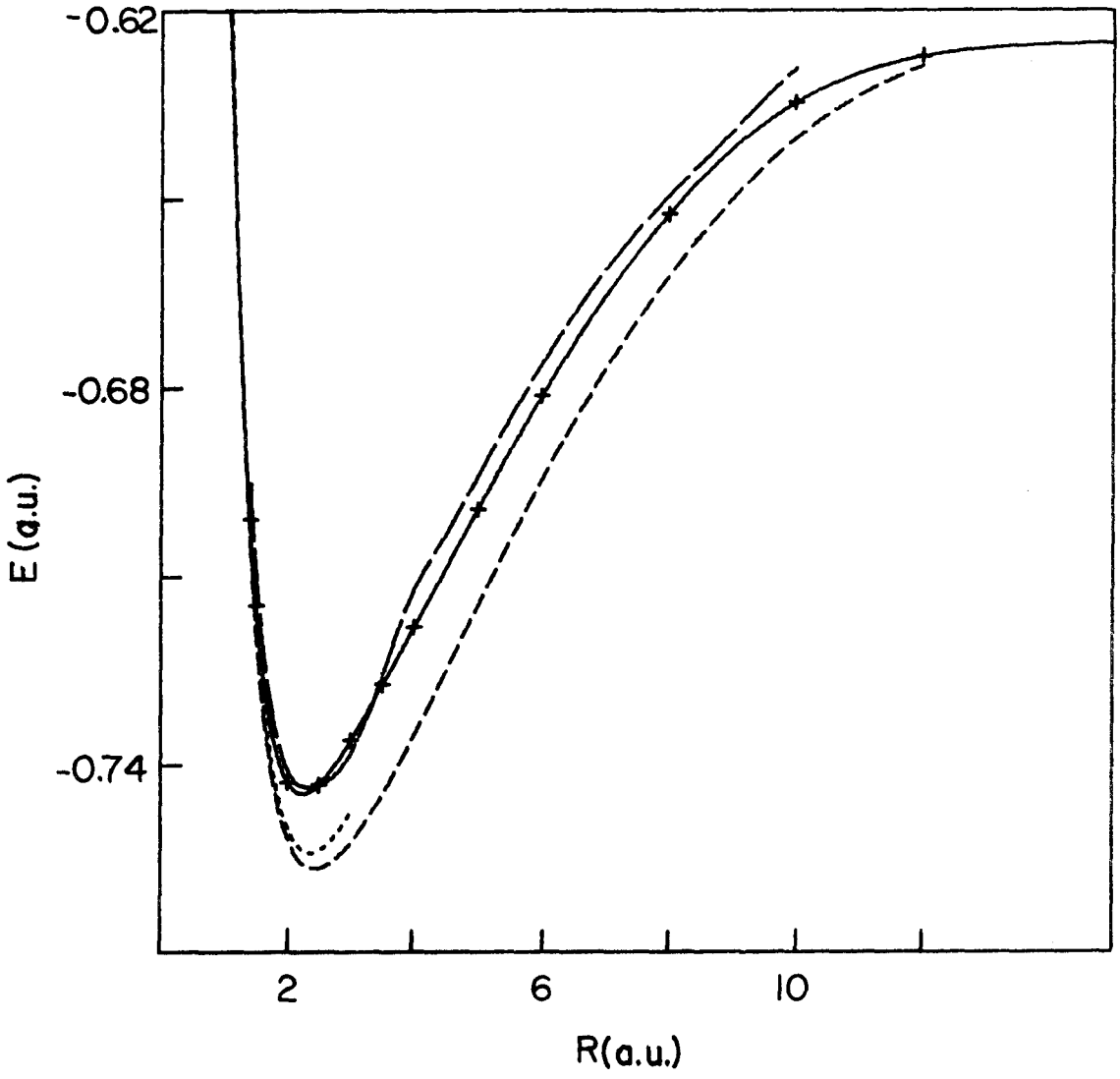


Fig. 22. Total energies for the $1\ ^1\Sigma_u^+$ state of H_2 (called B): long dashes, limited CI (Ref. 39); short dashes, more complete CI (Ref. 38); medium dashes, exact (Ref. 40); solid line and crosses, present calculation (16 basis functions).

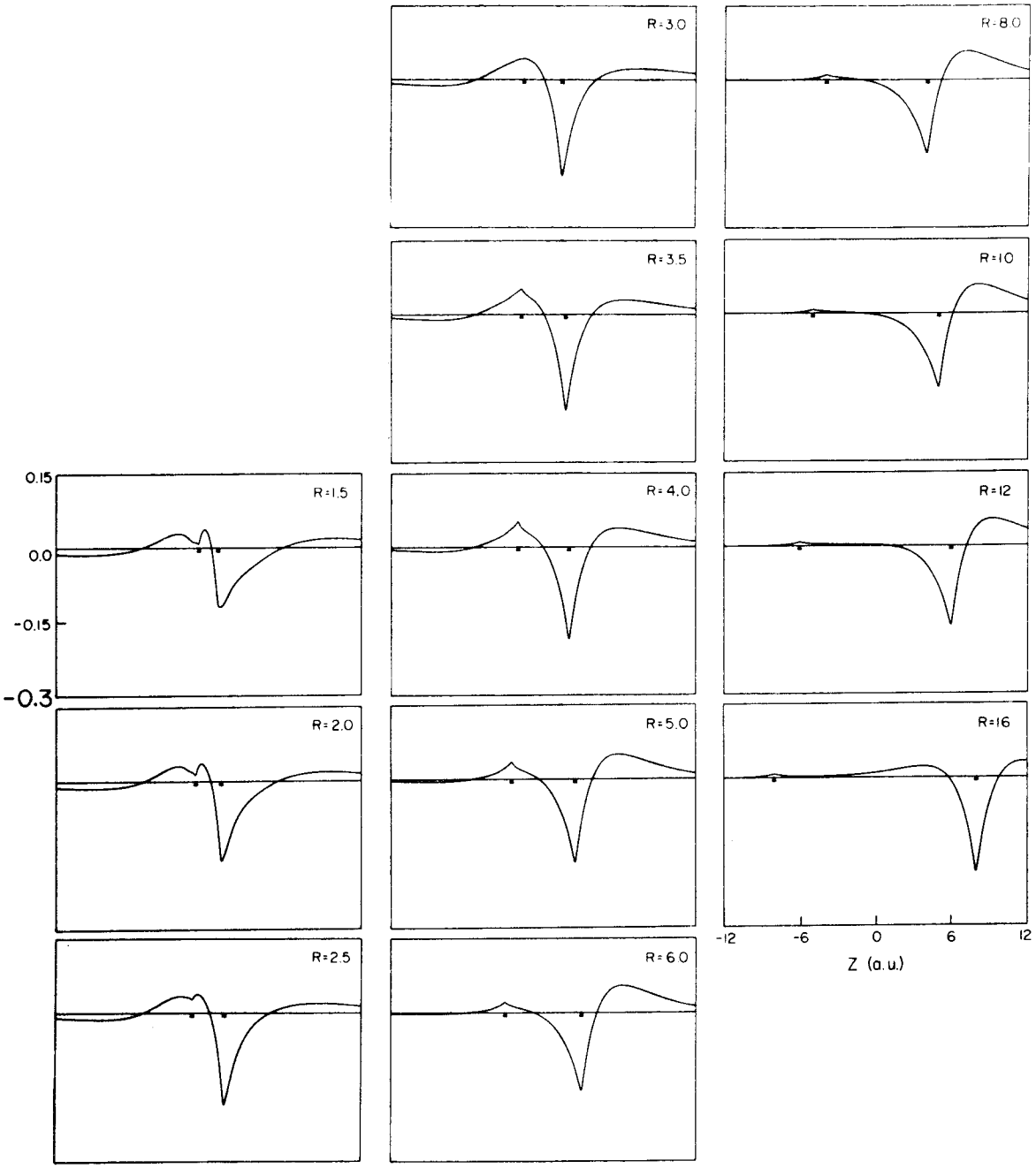


Fig. 23. φ_b orbitals for the 2 $^1\Sigma_u^+$ state of H_2; PGVB (16 basis functions).

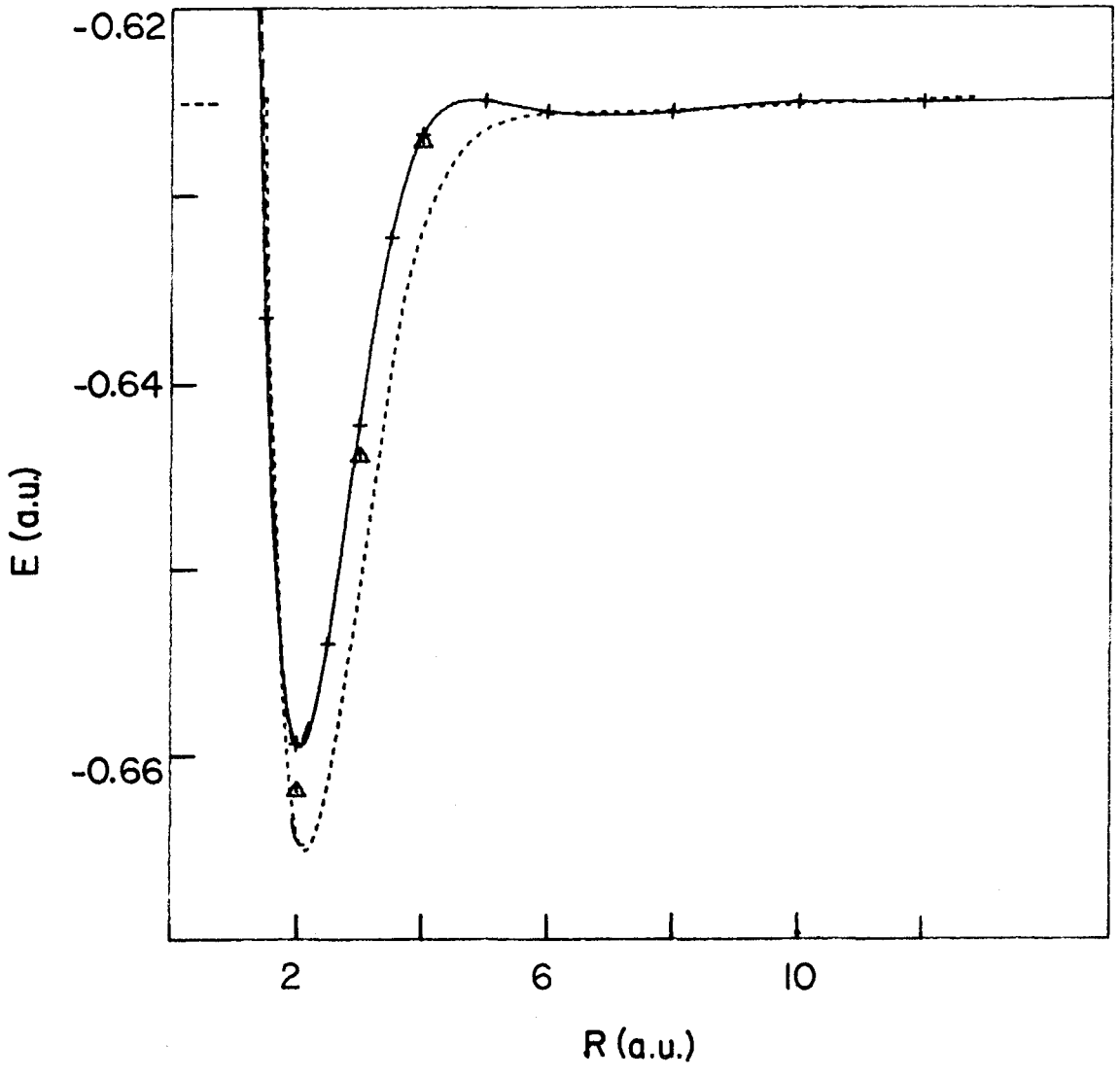


Fig. 24. Total energies for the 2 $^1\Sigma_u^+$ state of H_2 (called B′): medium dashes, HF (Ref. 41); short solid arc R = 1.9 to R = 2.1 CI (Ref. 36); short dashes, RKR (Ref. 42); solid line and crosses, present calculation (16 basis functions); triangles, present calculation (18 basis functions).

this hump will be sufficient to resolve the difficulties with the experimental curve.

The $^1\Sigma_u^+$ results are summarized in the plot of the orbital energies shown in Fig. 25.

The $^3\Sigma_g^+$ States:

The classification of the triplet states according to orbital character proceeds as smoothly and as informatively as for the singlets except for one important difference. The outer electron finds the already occupied proton to be repulsive. No triplet states of H^- are bound.

The first significant calculation on the a $^3\Sigma_g^+$ state of H_2 was that of James and Coolidge.[43] The MO configuration $1s\sigma 2s\sigma$ has been associated with this state. A glance at the orbital-line-plots in Fig. 26 convinces one of the appropriateness of this description. The potential curves are given in Fig. 27.

Wakefield and Davidson[37] first discussed the characters of the h $^3\Sigma_g^+$ and g $^3\Sigma_g^+$ states, identifying them respectively as $3s\sigma$ and $3d\sigma$ at very small R, mixed at R = 2 (they cross), and reversed [$3d\sigma$ and $3s\sigma$] at larger R. The orbitals are shown in Figs. 28, 29, and 30, the energies in Figs. 31 and 32. We may think of the hump in the 2 $^3\Sigma_g^+$ curve as being due to a promotional effect, the n = 2 orbital at large R becoming an n = 3 orbital at small R.

As before, the $^3\Sigma_g^+$ states are summarized in the plot of orbital energies, Fig. 33.

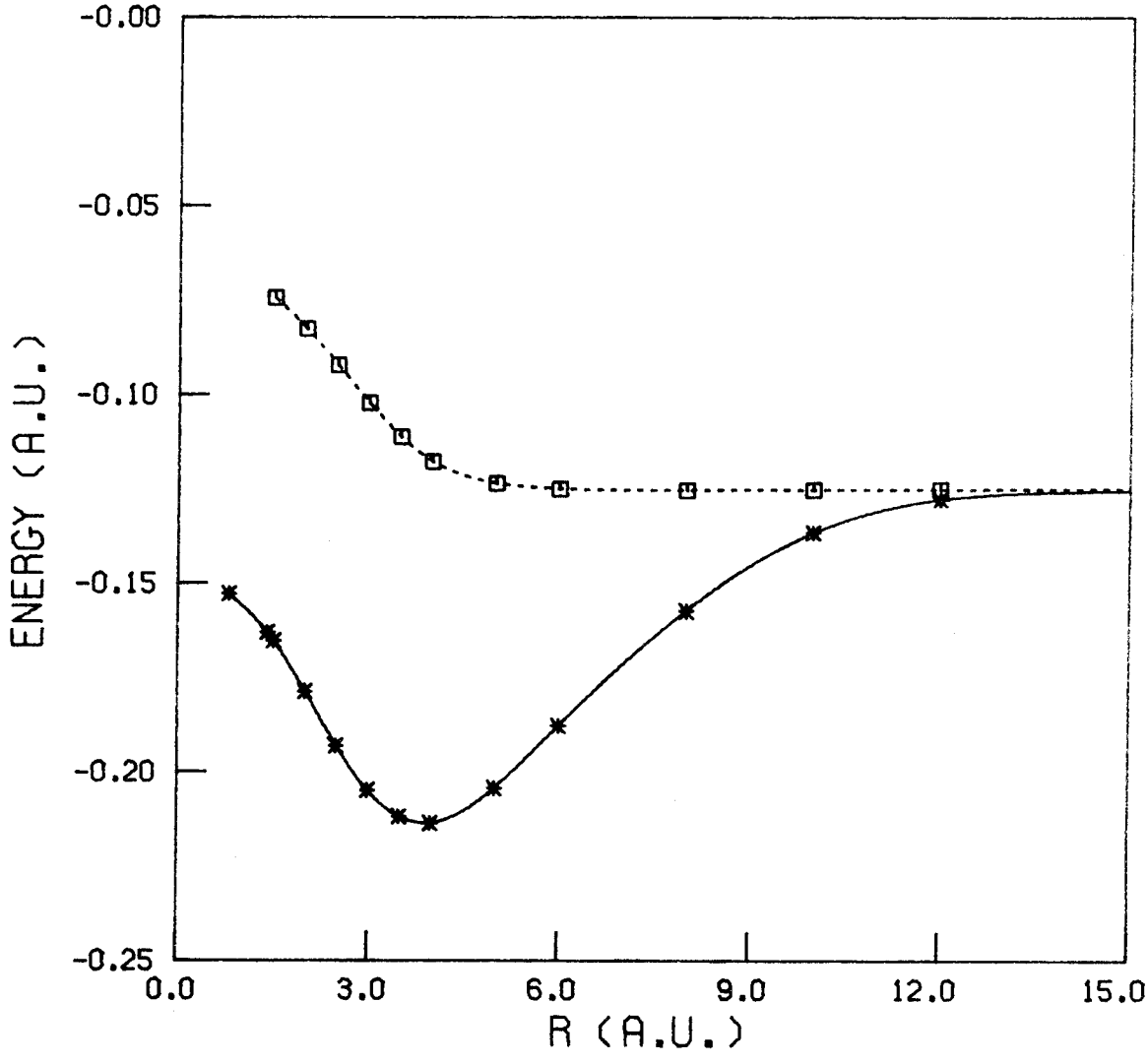


Fig. 25. PGVB orbital energies, ϵ_b, for $^1\Sigma_u^+$ states of H_2: solid line and asterisks, 1 $^1\Sigma_u^+$; short dashes and squares, 2 $^1\Sigma_u^+$.

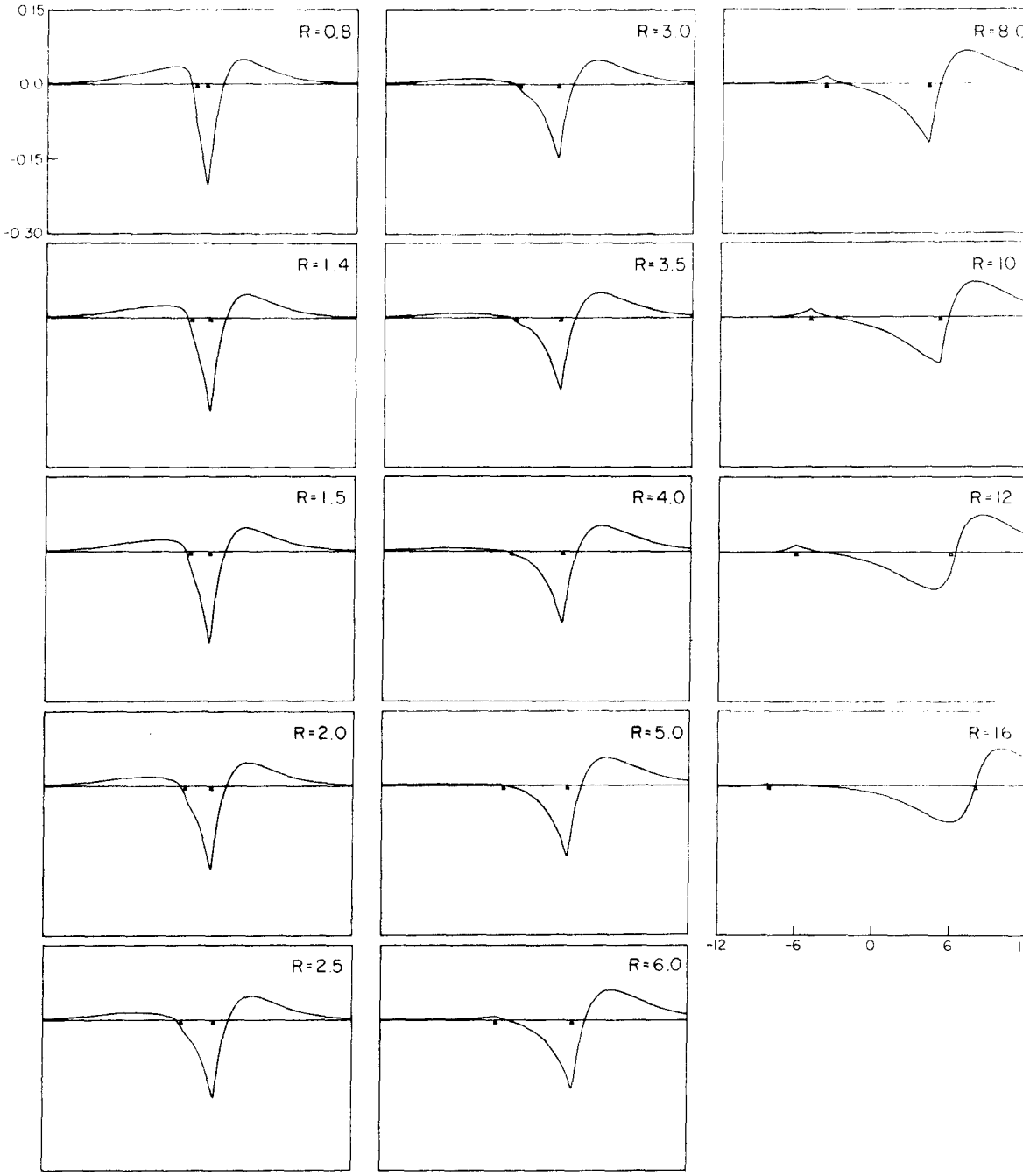


Fig. 26. φ_b orbitals for the $1\ ^3\Sigma_g^+$ state of H_2, PGVB (16 basis functions).

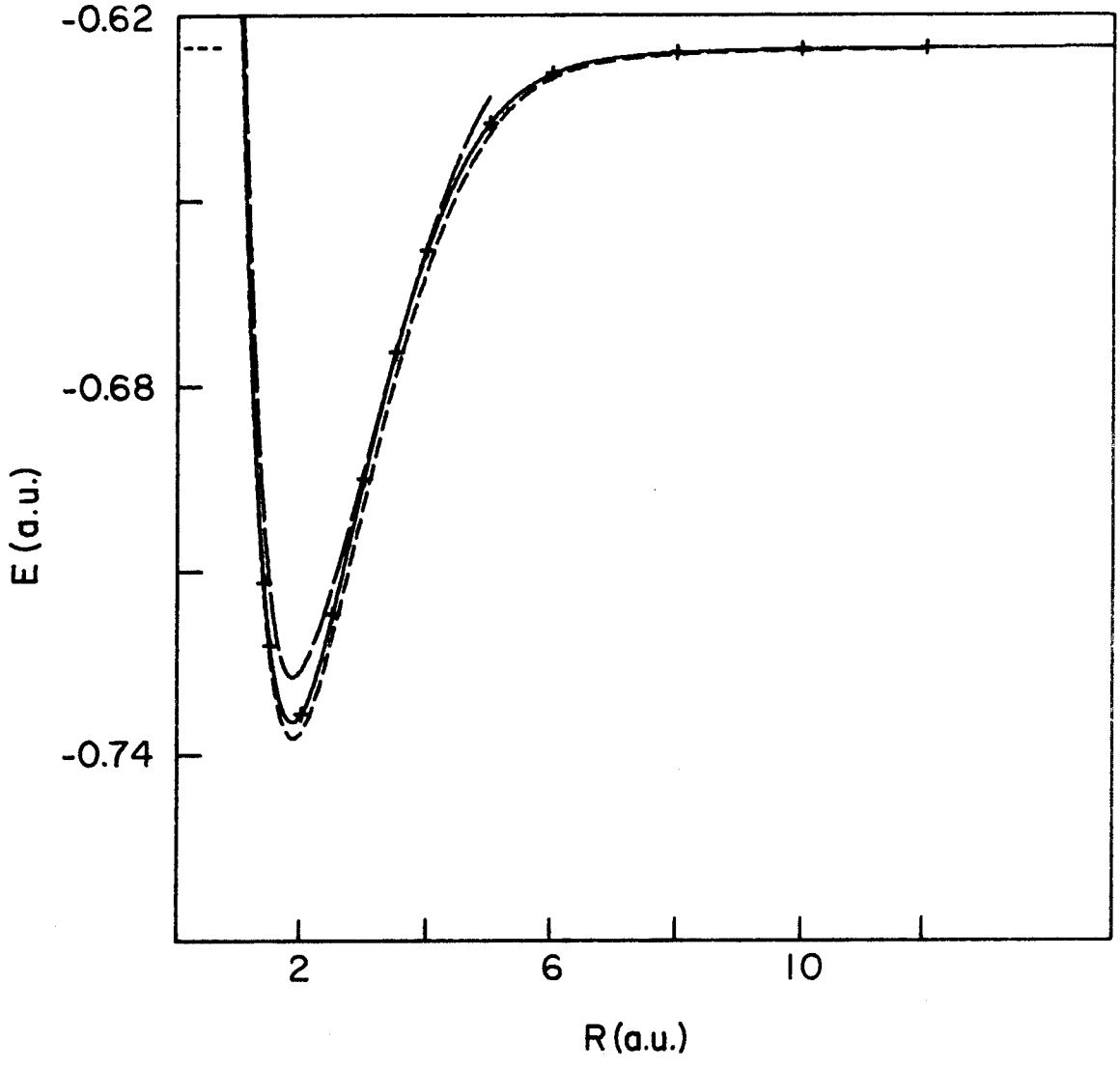


Fig. 27. Total energies for the $1\ ^3\Sigma_g^+$ state of H_2 (called a); long dashes, limited CI (Ref. 44), medium dashes, exact (Ref. 40b); solid line and crosses, present calculation (16 basis functions).

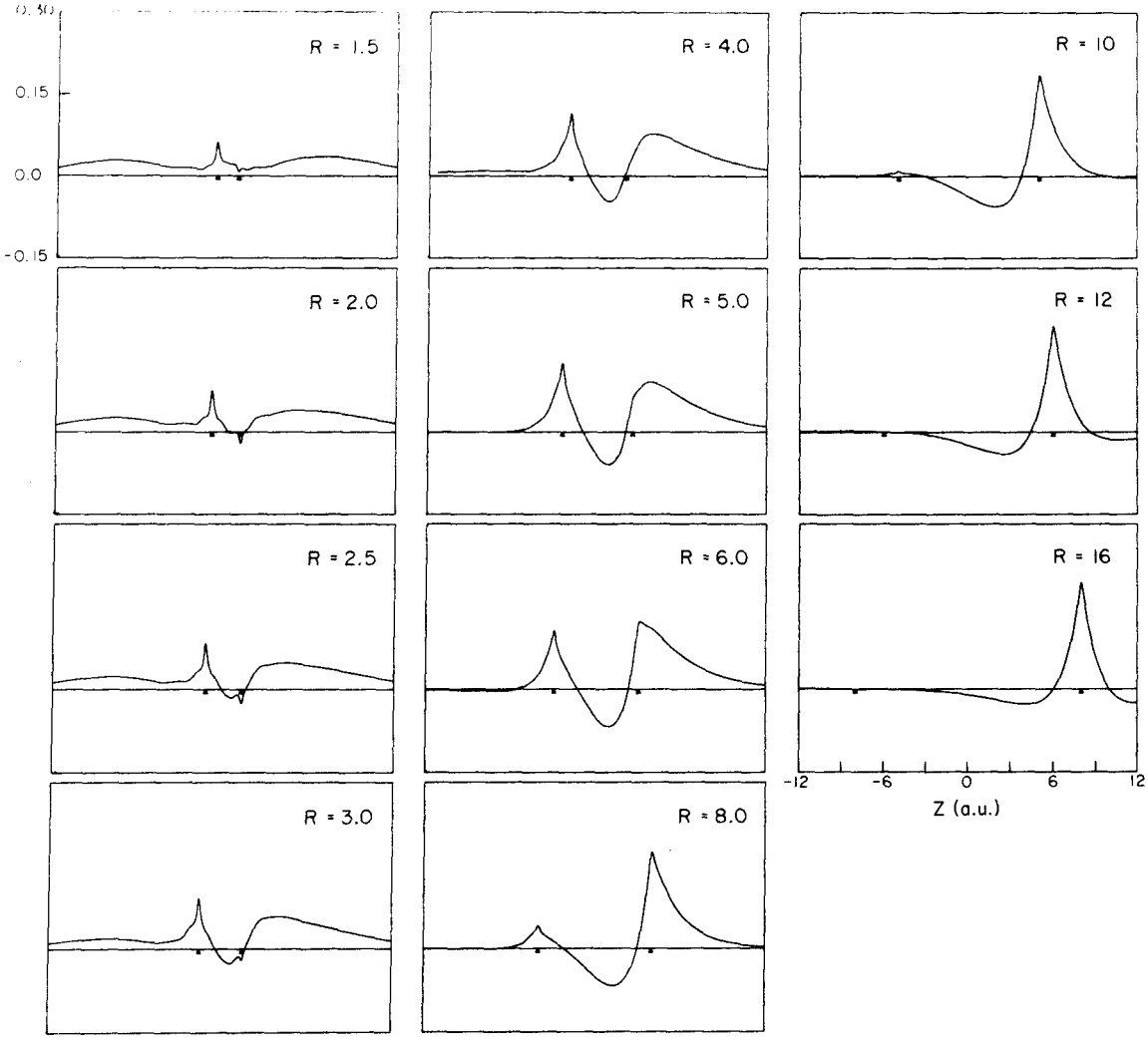


Fig. 28. φ_b orbitals for the 2 $^3\Sigma_g^+$ state of H_2; PGVB (16 basis functions).

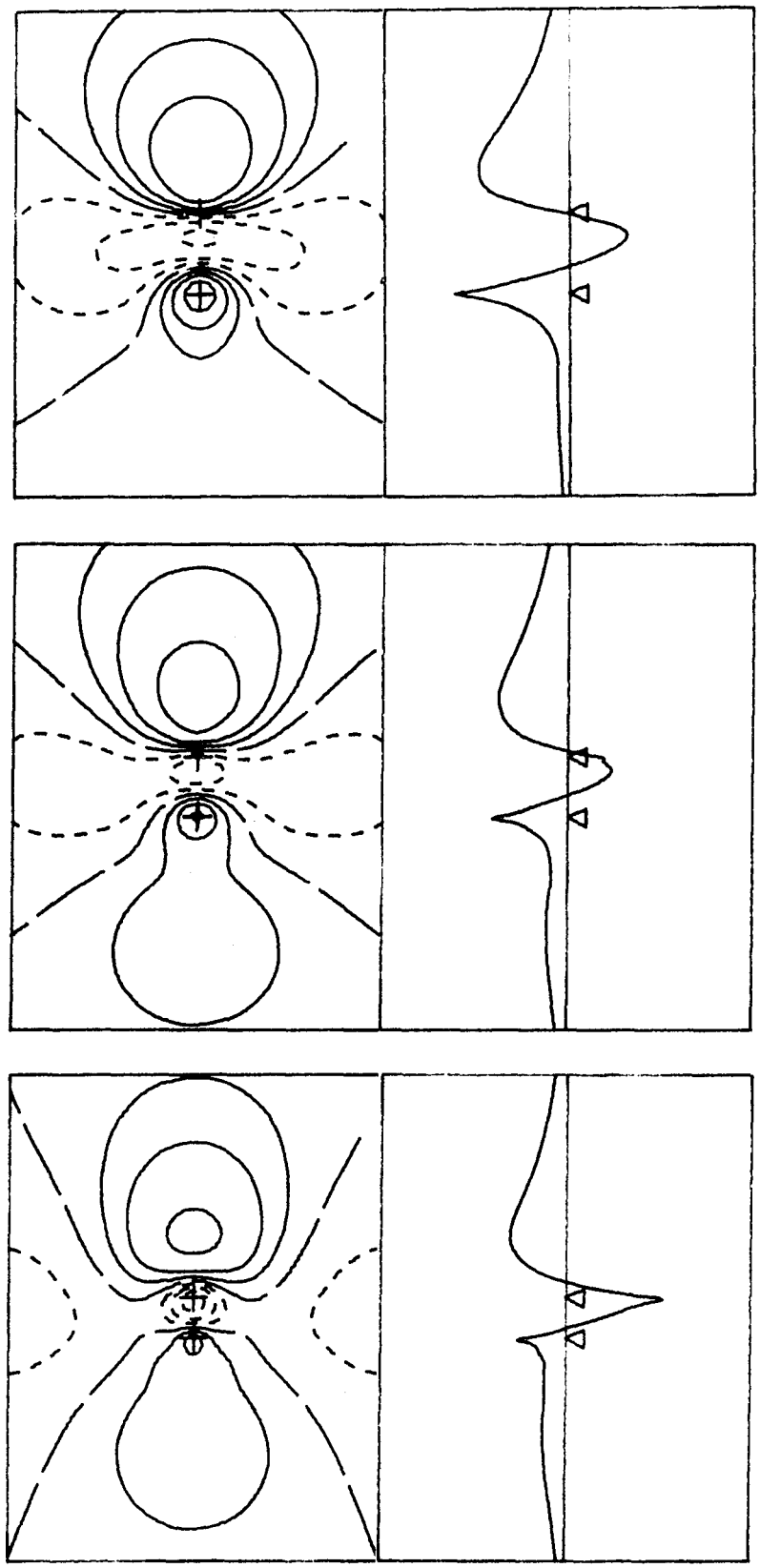


Fig. 29. φ_b orbitals for the $2\,^3\Sigma_g^+$ state of H_2; PGVB (18 basis functions); from left to right R = 2, 3, 4; horizontal scale ± 12 a.u.; vertical scale contour plot ± 9 a.u.; line plot ± 0.15 amplitude; contours 0, ± 0.01, ± 0.02, ± 0.04, ± 0.08.

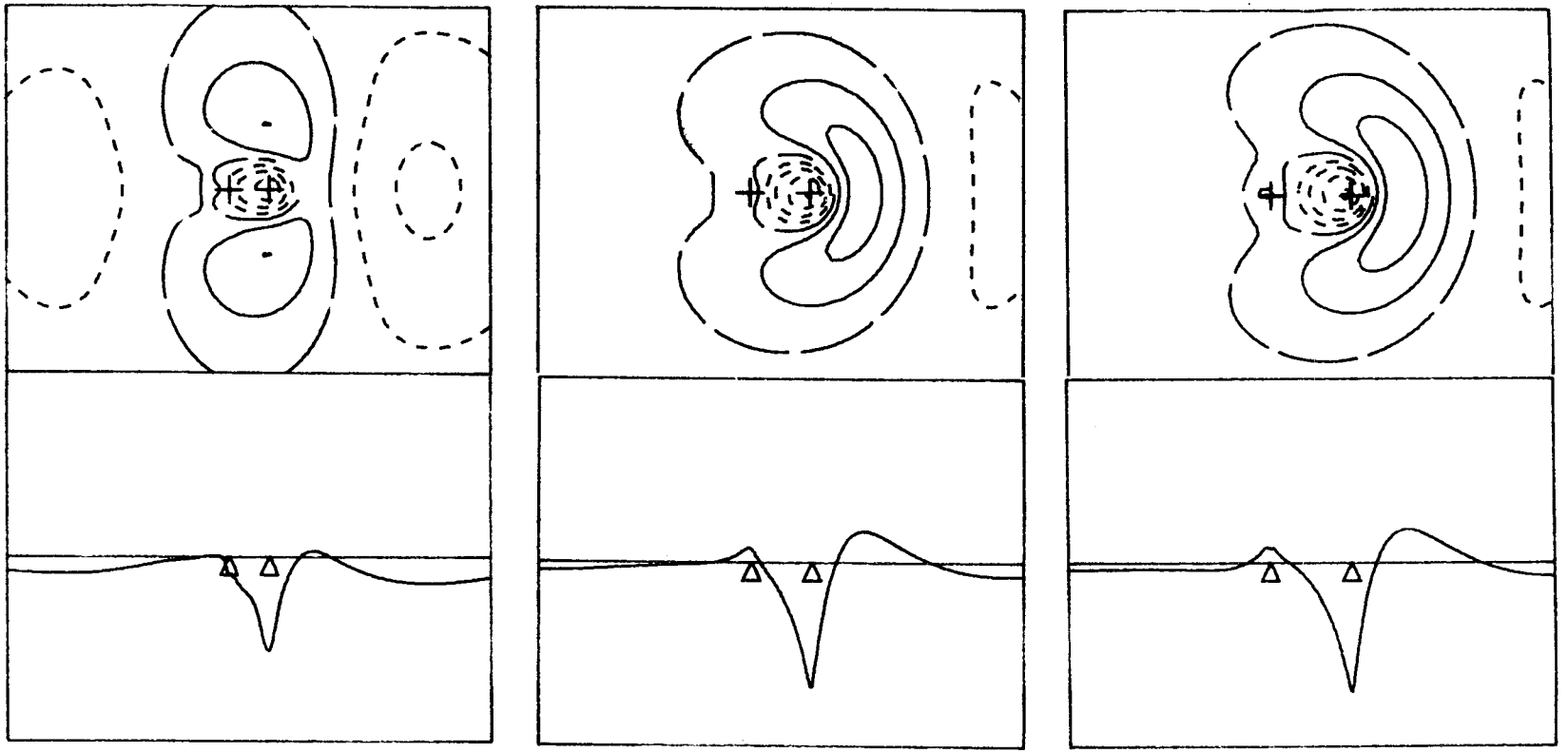


Fig. 30. φ_b orbitals for the 3 $^3\Sigma_g^+$ state of H_2; PGVB (18 basis functions); from left to right R = 2, 3, 4; horizontal scale ± 12 a.u.; vertical scale contour plot ± 9 a.u.; line plot ± 0.15 amplitude; contours 0, ± 0.01, ± 0.02, ± 0.04, ± 0.08.

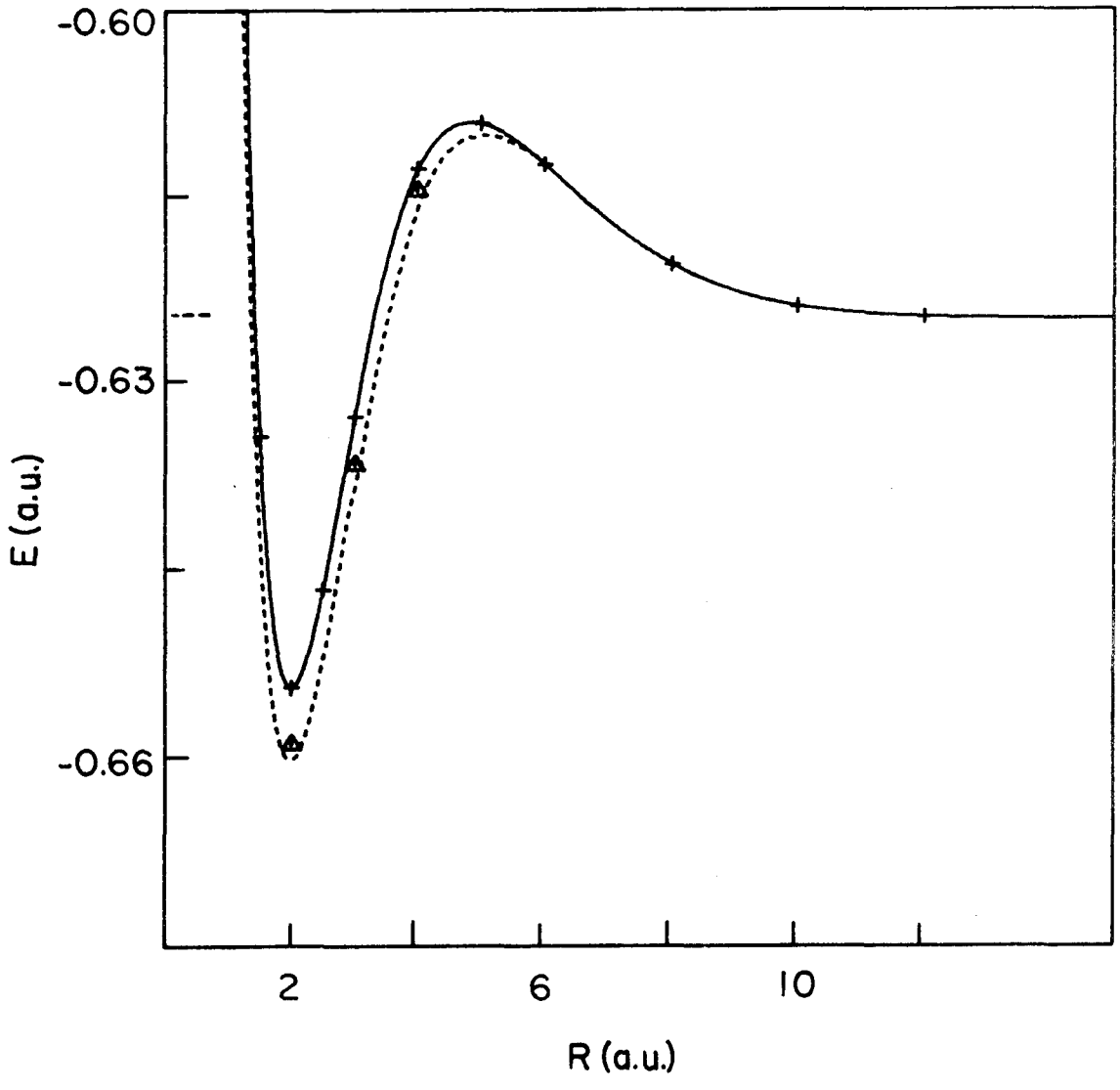


Fig. 31. Total energies for the 2 $^3\Sigma_g^+$ state of H_2 (called h): short dashes, CI (Ref. 37); solid line and crosses, present calculation (16 basis functions), triangles, present calculation (18 basis functions).

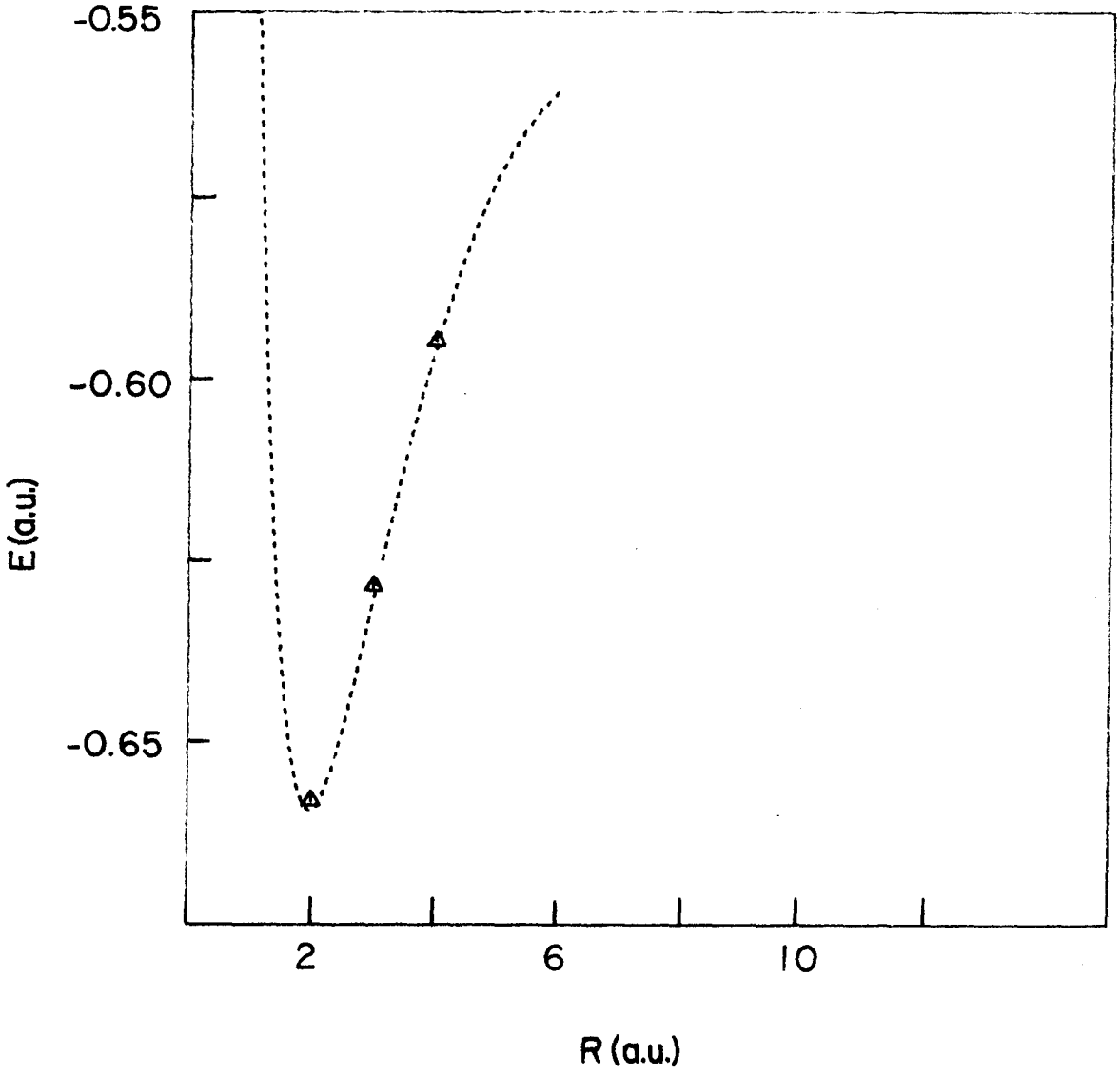


Fig. 32. Total energies for the 3 $^3\Sigma_g^+$ state of H_2 (called g): short dashes, CI (Ref. 37); triangles, present calculation (18 basis functions).

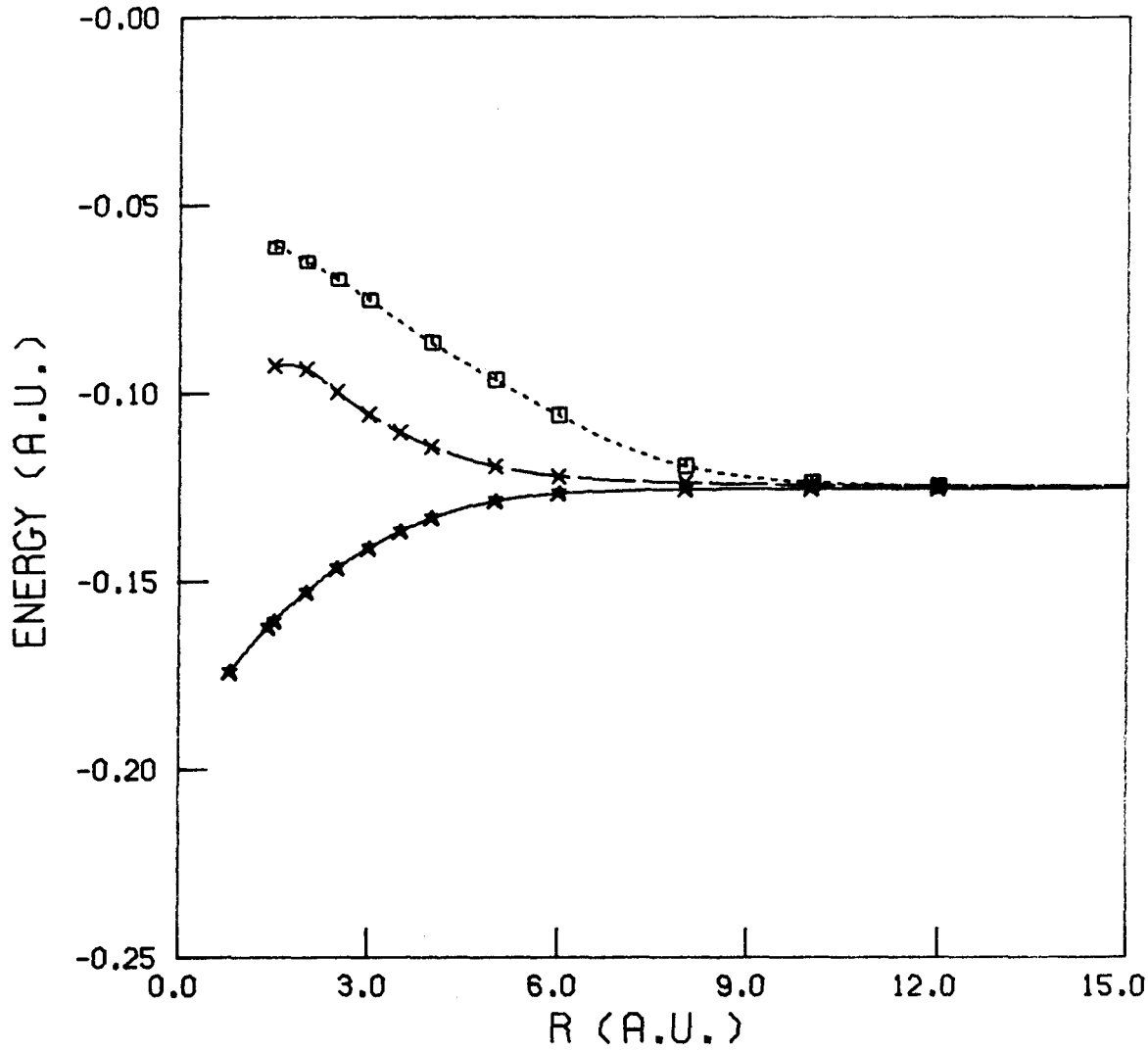


Fig. 33. PGVB orbital energies, ϵ_b, for $^3\Sigma^+$ states of H_2: solid line and stars, $1\ ^3\Sigma_g^+$; short dashes and squares, $2\ ^1\Sigma_g^+$; long dashes and x's, $2\ ^3\Sigma_u^+$.

The b $^3\Sigma_u^+$ state was the only one whose dissociation is adequately described by MO ideas. I prefer to think of this state as coming from the configuration

$$\boxed{1s\sigma_L\ 1s\sigma_R}_u \quad .$$

The wavefunction vanishes at small R unless the outer orbital becomes more and more antisymmetric. This is illustrated in the orbital-line-plots (Fig. 34). The repulsive energy curves are not shown (except in Fig. 2) since the Hartree-Fock, [31] exact, [32] and present projected calculated curves are visually indistinguishable.

As far as I can find, the e $^3\Sigma_u^+$ has received only the limited theoretical treatment from R = 1.9 to R = 2.0 a.u. of Rothenberg and Davidson. This curve, the experimental RKR curve of Dieke, [45] and the present PGVB curve are shown in Fig. 35. As we can see from the line-plots in Fig. 36, the φ_b orbital begins as $2s\sigma$ at large R, becoming $3p\sigma$ at small R. The orbital energy is shown in Fig. 33.

Summary: This entire description of the low-lying Σ states of H_2 is summarized in Table VII.

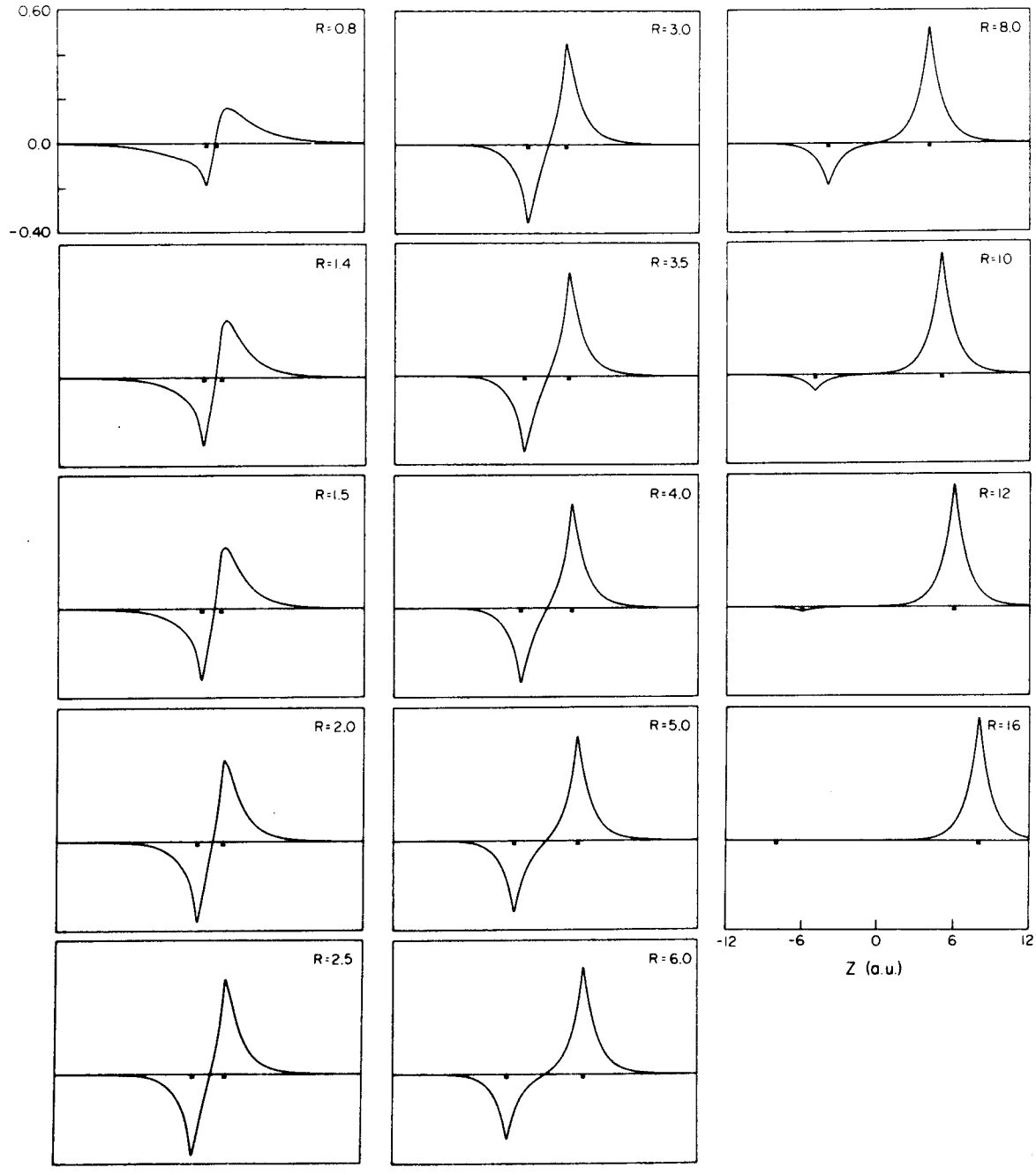


Fig. 34. φ_b orbitals for the $1\ ^3\Sigma_u^+$ state of H_2; PGVB (16 basis functions).

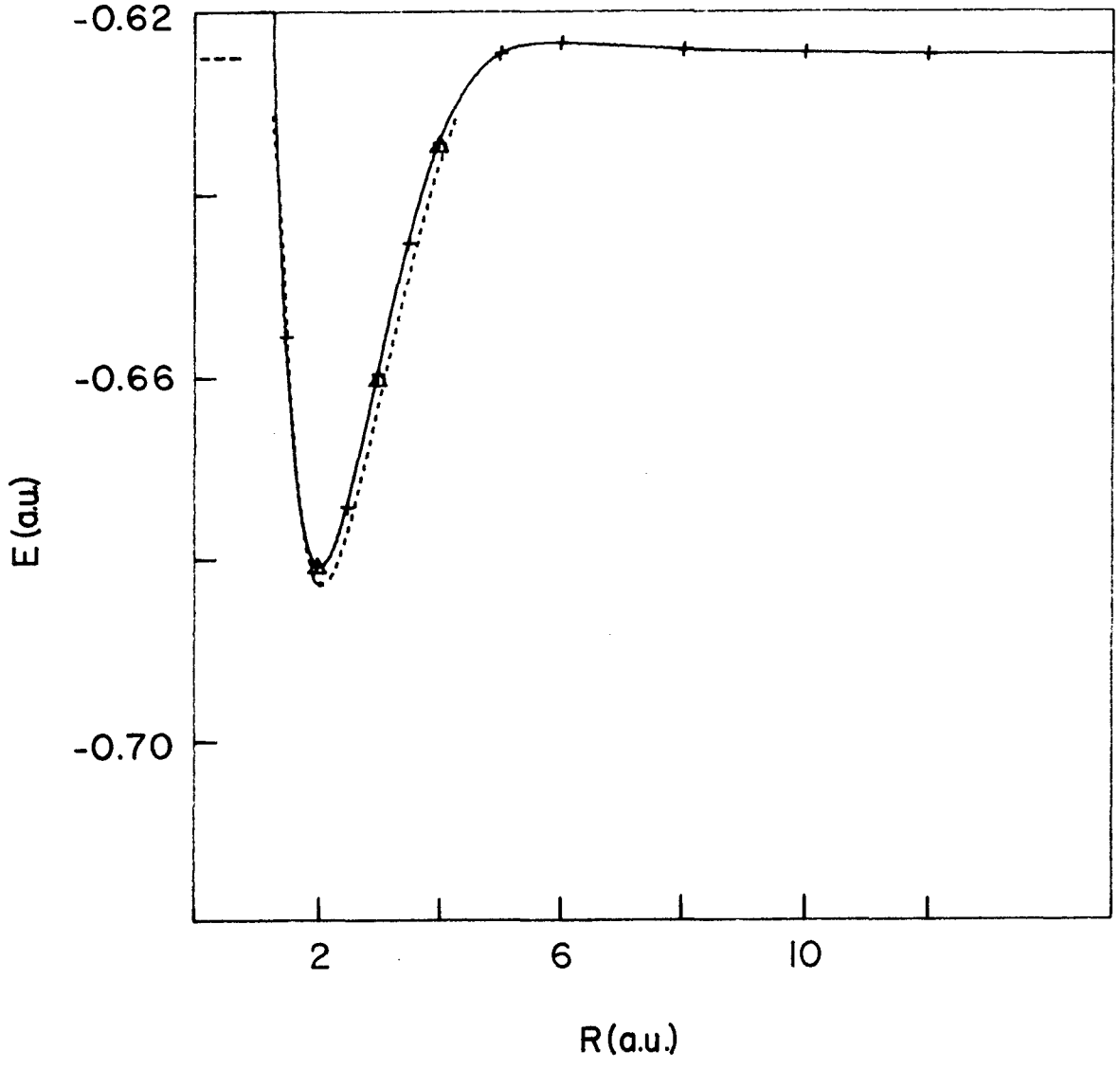


Fig. 35. Total energies for the 2 $^3\Sigma_u^+$ state of H_2 (called e); short solid arc from R = 1.9 to R = 2.1, CI (Ref. 36); short dashes, RKR (Ref. 45); solid line and crosses, present calculation (16 basis functions); triangles, present calculation (18 basis functions).

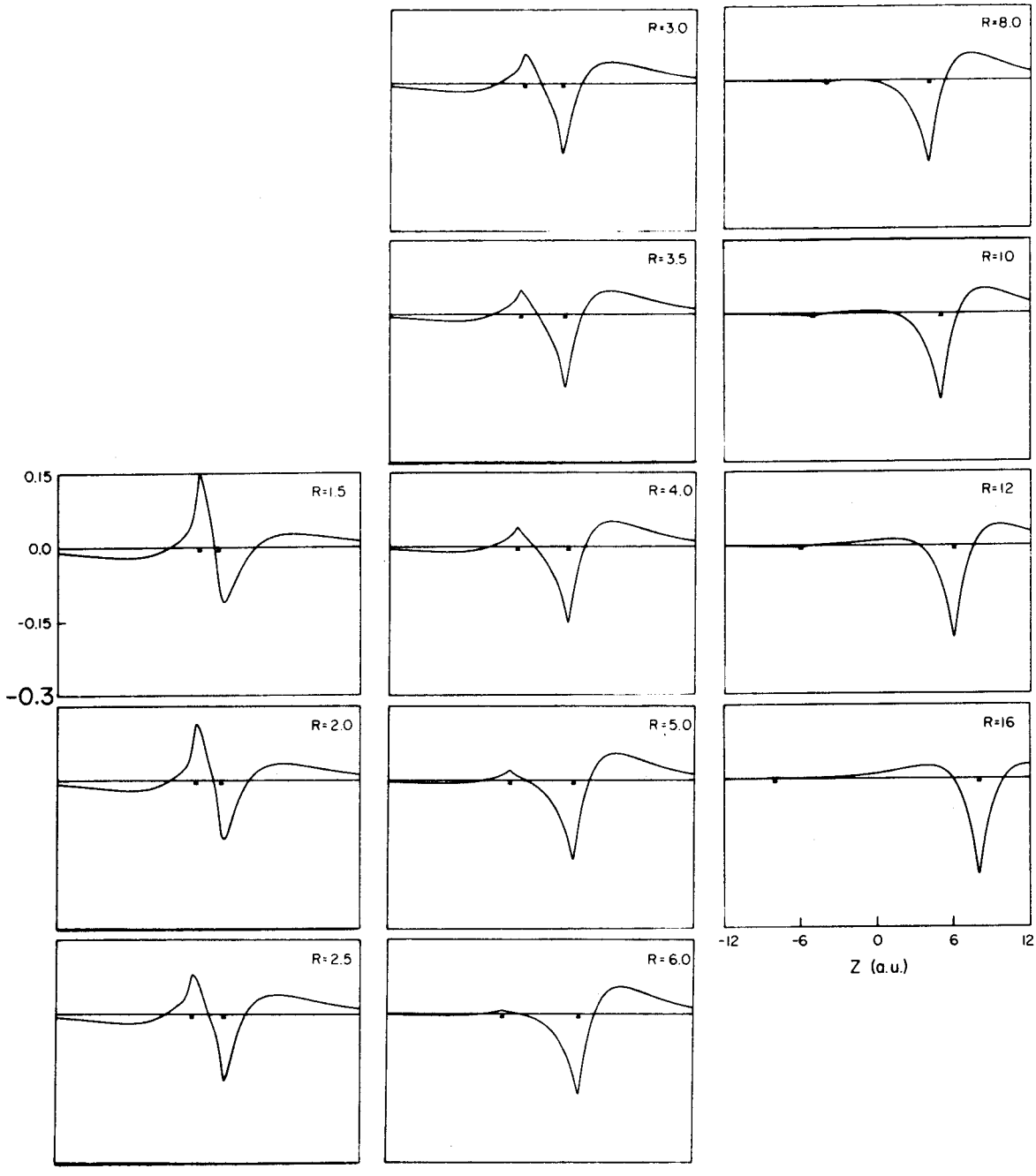


Fig. 36. φ_b orbitals for the 2 $^3\Sigma_u^+$ state of H_2; PGVB (16 basis functions).

TABLE VII. Summary of Orbital Characters.

State	φ_b		Features (in a.u.)
	Large R	$R \simeq 2$	
$1\ ^1\Sigma_g^+$ (X)	$1s\sigma$	$1s\sigma$	
$2\ ^1\Sigma_g^+$ (E, F)	$2p\sigma$	$2s\sigma$	minima (2, 4.5), hump (3)
$3\ ^1\Sigma_g^+$ (H)	$2s\sigma$	$3d\sigma$	minima (2, 3.5)
$4\ ^1\Sigma_g^+$ (G)	$3d\sigma$	$3s\sigma$	minima (2, 12?)
$1\ ^1\Sigma_u^+$ (B)	$2p\sigma$	$2p\sigma$	broad minimum
$2\ ^1\Sigma_u^+$ (B′)	$2s\sigma$	$3p\sigma$	shallow outer minimum (8)
$1\ ^3\Sigma_g^+$ (a)	$2s\sigma$	$2s\sigma$	
$2\ ^3\Sigma_g^+$ (h)	$3d\sigma$ (n = 2)	$3s\sigma \pm 3d\sigma$	hump (5)
$3\ ^3\Sigma_g^+$ (g)	$3s\sigma$ (?)	$3d\sigma \pm 3s\sigma$	
$1\ ^3\Sigma_u^+$ (b)	$1s\sigma$	$2p\sigma$	
$2\ ^3\Sigma_u^+$ (e)	$2s\sigma$	$3p\sigma$	hump (6)

IMPLICATIONS

We have seen the success with which spatial projection permits a description of the excited states of H_2, in spite of the molecular symmetry. This independent-particle model explains the potential curves without the need for interaction between configurations. Rather, the various minima and maxima are due to changes in orbital character. The orbital characters themselves come from the model one-electron heteronuclear diatomics.

The applicability of orbital character extends far beyond the states of H_2. Recent detailed discussions of the excited states of LiH,[46] He_2,[8k, 30] and LiNa[47] may be examined. The outer orbital for most small diatomics very closely resembles one of the states of the model one-electron heteronuclear diatomic. One might conclude that an orbital is an orbital is an orbital.

Symmetry projection has become more attractive for much larger systems as well. A description of the states of ozone, for example, would be much clarified by symmetry-projected GVB calculations. One state of interest involves a lone σ electron on one end and a lone π electron on the other.[48] The MO theory is rather overwhelmed by such a state. A similar situation obtains in a discussion of excitations in solids. With such high symmetry, it seems a shame to let it go to waste, but the only way I can think of to treat localized excitations consistently requires a spatial projection operator.

It is only after considerable education that group theoretical ideas become intuitive. At that point the group theory may begin to overwhelm what old-fashioned physical intuition remains. One should remember that while group theory and symmetry make the problems easier, they sometimes make them so easy that we deceive ourselves. Perhaps we should trust the 'exact' symmetry less and our naive intuition more, in spite of calculational difficulties.

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2. G. Herzberg, Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules (D. Van Nostrand, Princeton, N. J., 1966), p. 398.
3. Best in the sense of lowest many-electron energy, which by the variational principle is expected to give a good approximation to the ground state wavefunction.
4. R. J. Buenker, J. L. Whitten, and J. D. Petke, J. Chem. Phys. 49, 2261 (1968).
5. For totally symmetric, nondegenerate, singlet states (the common case for molecular ground states), the Hartree-Fock orbitals must be basis functions for the irreducible representations of the spatial symmetry group (i.e., symmetry functions). For a proof, see C. C. J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
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7. The idea of Generalized Valence Bond calculations is to choose the form of the wavefunction to resemble that of simple valence bond, but then to optimize the orbitals self-consistently as in Hartree-Fock. The names GVB and GI are used interchangeably

herein. Several calculations have been done with various modifications and restrictions. A few of these are listed below.

Maximal Pairing (G1, MPHF)

7a) E. R. Davidson and L. L. Jones, J. Chem. Phys. 37, 1918 (1962).

7b) W. A. Goddard III, Phys. Rev. 169, 120 (1968).

7c) W. E. Palke and W. A. Goddard III, J. Chem. Phys. 50, 4524 (1969).

7d) U. Kaldor and F. E. Harris, Phys. Rev. 183, 1 (1969).

7e) R. J. Blint, W. A. Goddard III, R. C. Ladner, and W. E. Palke, Chem. Phys. Letters 5, 302 (1970).

Orthogonal Pairs (GVB, separated pairs)

7f) P. J. Hay, W. J. Hunt, and W. A. Goddard III, Chem. Phys. Letters 13, 30 (1972).

7g) W. J. Hunt, P. J. Hay, and W. A. Goddard III, J. Chem. Phys. 57, 738 (1972) and references cited therein.

Spin Polarized (GF, DODS, SEHF)

7h) W. A. Goddard III, Phys. Rev. 157, 81 (1967).

7i) W. A. Goddard III, J. Chem. Phys. 48, 1008 (1968).

7j) U. Kaldor, Phys. Rev. 176, 19 (1968).

7k) S. L. Guberman and W. A. Goddard III, J. Chem. Phys. 53, 1803 (1970).

Spin-Coupling Optimized (SOGI, SOSCF)

7ℓ) R. C. Ladner and W. A. Goddard III, J. Chem. Phys. 51, 1073 (1969).

7m) U. Kaldor, Phys. Rev. A 1, 1586 (1970); see also Ref. 7d.

7n) W. A. Goddard III and R. C. Ladner, J. Am. Chem. Soc. 93, 6750 (1971).

8. The ideas of symmetry projected orbital products have been developed and in some cases used by a number of workers.

General Projection (spin and space)

8a) P.-O. Löwdin, Phys. Rev. 97, 1474 (1955).

8b) P.-O. Löwdin, Rev. Mod. Phys. 34, 520 (1962).

8c) P.-O. Löwdin,"The Projected Hartree-Fock Method" in Quantum Theory of Atoms, Molecules, and Solids, P.-O. Löwdin, Ed. (Academic Press, New York, 1966), p. 601.

8d) C. F. Bunge, Phys. Rev. 154, 70 (1967).

8e) G. A. Gallup, J. Chem. Phys. 48, 1752 (1968).

Permutation Projection (see Ref. 7)

Spin Projection (calculations)

8f) S. Lunell, Phys. Rev. A 1, 360 (1970).

8g) S. Lunell, Chem. Phys. Letters, 13, 93 (1972); see also Ref. 8d.

Spatial Projection (calculations)

8h) R. C. Morrison and G. A. Gallup, J. Chem. Phys. 50, 1214 (1969).

8i) D. L. Huestis, T. H. Dunning, Jr., and W. A. Goddard III, Bull. Am. Phys. Soc. 14, 1192 (1969).

8j) W. T. Zemke, P. G. Lykos, and A. C. Wahl, J. Chem. Phys. 51, 5635 (1969).

8k) S. L. Guberman and W. A. Goddard III, Chem. Phys. Letters 14, 460 (1972).

8ℓ) D. L. Huestis and W. A. Goddard III, Chem. Phys. Letters 15, 000 (1972) in which some of the work reported in this thesis has already been published.

9. That is, commutative, one operator in each class and only non-degenerate one-dimensional representations. See also Ref. 10, p. 7.

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11. See also Appendix I.

12. Reference 17, Chap. II, Sec. 11.

13. Reference 10, pp. 147-150.

14. We take the plus sign for a singlet and the minus sign for a triplet. The spin part of the wavefunction factors out for two electrons. The sign is chosen to satisfy the Pauli principle.

15. O_{ii} is the permutation projector for the spatial orbitals, and $d\tau'_j$ indicates that the coordinates of electron j are omitted from the integration. See also Ref. 7h.

16. Φ'_k means Φ with orbital φ_k removed.

17. See, for example, W. A. Goddard III, Class Notes for Chemistry 226a, "Advanced Topics in Quantum Chemistry," California Institute of Technology, Winter Term, 1969 (unpublished). Chap. I, for the usual discussion.

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21. See, for example, Ref. 1, p. 329

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APPENDIX I.

Index Symmetry and the Transformation of Two-Electron Integrals

This Appendix discusses the general transformation of two-electron integrals and in specific the use of the index symmetry of the arrays of integrals to speed up the transformation.

INTRODUCTION

The calculation of molecular wavefunctions is often much facilitated by the transformation of the fundamental two-electron integrals

$$A_{ij,\,k\ell} \equiv \langle \psi_i(1)\psi_k(2) \left| \frac{1}{r_{12}} \right| \psi_j(1)\psi_\ell(2) \rangle$$

$$\equiv \int d^3x_1 \psi_i(1)\psi_j(1) \int d^3x_2 \frac{1}{r_{12}} \psi_k(2)\psi_\ell(2) \qquad (1)$$

into the corresponding two electron integrals over a new set of basis functions

$$Z_{\alpha\beta,\,\gamma\delta} \equiv \langle \phi_\alpha(1)\phi_\gamma(2) \left| \frac{1}{r_{12}} \right| \phi_\beta(1)\phi_\delta(2) \rangle \,, \qquad (2)$$

where each ϕ_α is a linear combination of the ψ_i's.

If the number of basis functions in the two sets is N, then depending on how the Z integrals are calculated in terms of the A integrals, the number of multiplications (or the OpC [1]) may increase as rapidly as qN^8 or as slowly as $q'N^5$. In addition, the coefficients q and q′ may vary by more than a factor of three depending on the specific approach chosen.

Herein we will consider in detail the techniques for such transformations. In particular we note that the array of integrals $\hat{A}$ is symmetric in the indices i and j; and the indices k and ℓ; and in the pairs ij and kℓ. This index symmetry can be exploited during the transformation, in order to minimize the multiplicative coefficient q.

MATRICES

First we will consider the simpler case of a given symmetric N by N matrix $\underset{\sim}{X}$, which is to be transformed to a symmetric M by M matrix $\underset{\sim}{Y}$, defined as

$$Y_{\alpha b} = \sum_{ij} C_{i\alpha} X_{ij} C_{j\beta}$$

or

$$\underset{\sim}{Y} = \underset{\sim}{C}^{t} \underset{\sim}{X} \underset{\sim}{C} \tag{3}$$

Here $\underset{\sim}{C}$ is a given N × M transformation matrix.

A. Direct multiplication: An obvious but inefficient method of accomplishing the transformation (3) would be to calculate the quantity $C_{i\alpha} X_{ij} C_{j\beta}$ for each i, j, α, and β. Each of these terms would then be accumulated in the appropriate $Y_{\alpha\beta}$. This technique would require $2N^2M^2$ multiplications. Use of the index symmetry of $\underset{\sim}{X}$ and $\underset{\sim}{Y}$ reduces the operation count to $\frac{1}{2}N(N+1)M(M+1)$.

B. Intermediate matrix: The direct multiplication method can be much improved simply by summing over j first, defining an intermediate matrix

$$(\underset{\sim}{X}\underset{\sim}{C})_{i\beta} = \sum_{j} X_{ij} C_{j\beta} \quad . \tag{4}$$

Then finally

$$Y_{\alpha\beta} = \sum_{i} C_{i\alpha} (\underset{\sim}{X}\underset{\sim}{C})_{i\beta} \quad . \tag{5}$$

Now N^2M multiplications are required in eq. (4) and $\frac{1}{2}NM(M+1)$ [i.e., $\alpha \geq \beta$] in eq. (5) for a total of $N^2M + \frac{1}{2}NM(M+1)$. This becomes almost $3/2\ N^3$ for $N = M \gg 1$ and only N^2M for $N \gg M$.

C. Index Symmetry: We notice that any symmetric matrix may be written as the sum of a matrix and its transpose:

$$\underset{\sim}{X} = \underset{\sim}{L} + \underset{\sim}{L}^{t} \quad . \tag{6}$$

This can be accomplished in an arbitrary number of ways. If we require $\underset{\sim}{L}$ to be lower triangular, then $\underset{\sim}{L}^{t}$ is upper triangular, and the decomposition is unique.

Using (6), Y can be written as

$$\underset{\sim}{Y} = \underset{\sim}{C}^{t}\underset{\sim}{L}\underset{\sim}{C} + \underset{\sim}{C}^{t}\underset{\sim}{L}^{t}\underset{\sim}{C}$$

or

$$\underset{\sim}{Y} = \underset{\sim}{C}^{t}\underset{\sim}{L}\underset{\sim}{C} + \left[\underset{\sim}{C}^{t}\underset{\sim}{L}\underset{\sim}{C}\right]^{t} \quad . \tag{7}$$

Since $\underset{\sim}{L}$ is lower triangular, the intermediate matrix

$$(\underset{\sim}{L}\underset{\sim}{C})_{i\beta} = \sum_{j=1}^{i} L_{ij}C_{j\beta} \tag{8}$$

will consume only $\frac{1}{2}$ N (N+1) M multiplications. The sum over i now requires NM^2 multiplications, so that the total OpC is $\frac{1}{2}$ N (N+1) M + NM^2. This reduces to 3/2 N^3 for N = M $\gg$ 1 and to $\frac{1}{2}$ N^2M for N $\gg$ M. Since N is almost always at least as large as M, it is apparent that this is the method of choice.

TWO-ELECTRON INTEGRALS

The two electron integrals of equations (1) and (2) are related by

$$Z_{\alpha\beta\gamma\delta} = \sum_{ijk\ell} C_{i\alpha}C_{j\beta}A_{ijk\ell}C_{k\gamma}C_{\ell\delta} \tag{9}$$

where $\underset{\sim}{C}$ is the N × M transformation matrix connecting the N functions $\{\psi_i\}$ and M functions $\{\phi_{\alpha}\}$.

A. Direct multiplication: As before the explicit calculation of $C_{i\alpha}C_{j\beta}A_{ijk\ell}C_{k\gamma}C_{\ell\delta}$ for each i, j, k, ℓ, α, β, γ, δ requires the largest number of operations, $\sim \frac{1}{2} N^4 M^4$, if the index symmetry of Z is used.

B. Density matrices: One method of improving upon direct multiplication is to use density matrices, which are defined by

$$D_{ij,\,\alpha\beta} = \begin{cases} [C_{i\alpha}C_{j\beta} + C_{i\beta}C_{j\alpha}] & i \neq j \\ C_{i\alpha}C_{j\beta} & i = j \end{cases} \qquad (10)$$

$$\text{for all } i \geq j,\ \alpha \geq \beta$$

Then eq. (9) becomes

$$Z_{\alpha\beta\gamma\delta} = \sum_{i\geq j} \sum_{k\geq \ell} D_{ij\alpha\beta}A_{ijk\ell}D_{k\ell\gamma\delta} \cdot \qquad (11)$$

Considering each pair i, j as a single subscript, ij = i(i-1)/2 + j, and similarly for $\alpha\beta$, and setting ms = $\frac{1}{2}$ M (M+1), ns = $\frac{1}{2}$ N (N+1), we obtain

$$Z_{\alpha\beta,\,\gamma\delta} = \sum_{ij=1}^{ns} \sum_{k\ell=1}^{ns} D_{ij,\,\alpha\beta}A_{ij,\,k\ell}D_{k\ell,\,\gamma\delta} \qquad (12)$$

This is just the conjugation of a symmetric matrix, and therefore requires at least $\frac{1}{2}$ ns (ms+1) ms + ns $(ms)^2$ multiplications. Expanding in terms of N and M, the OpC is 1/16 N (N+1)(N^2+N+2)M(M+1) + $\frac{1}{8}$N(N+1)M^2(M+1) or approximately 1/16 N^4M^2 + $\frac{1}{8}$ N^2M^4. This becomes 3/16 N^6 if N = M and 1/16 N^4M^2 if N $\gg$ M (see also Ref. [2]).

C. Intermediate matrices: Just as with the conjugation of matrices, we can obtain an alternative approach by saving the intermediate result after each summation

$$Z_{\alpha\beta\gamma\delta} = \sum_i C_{i\alpha} \sum_j C_{j\beta} \sum_k C_{k\gamma} \sum_\ell A_{ijk\ell} C_{\ell\delta} \qquad (13)$$

Using no index summetry, this takes $N^4M + N^3M^2 + N^2M^3 + NM^4$ multiplications, which leads to dominant terms of $4N^5$ and N^4M for N = M $\gg$ 1 and N $\gg$ M, respectively (see also Ref. [3]). Using the index symmetry of each intermediate result, i.e., never calculating anything more than once,reduces the OpC to $\frac{1}{2}$ N^4M + $\frac{1}{4}$ N^3M^2 + $\frac{1}{2}$ N^2M^3 + $\frac{1}{8}$ NM^4 which reduces to $1\frac{3}{8}$ N^5 and $\frac{1}{2}$ N^4M for N = M $\gg$ 1 and N $\gg$ M, respectively.

D. Index symmetry: The given problem (9) can be written in symbolic tensor notation

$$\hat{Z} = \underset{\sim}{C}^t \otimes \underset{\sim}{C}^t \cdot \hat{A} \cdot \underset{\sim}{C} \otimes \underset{\sim}{C} \quad . \qquad (14)$$

Let $\hat{Q}$ be any fourth rank tensor, then the possible index permutations (analogous to matrix transposition) are defined by

$$\hat{Q}^{\tau}_{ijk\ell} = \hat{Q}_{\tau(ijk\ell)} \tag{15}$$

where τ is any permutation from S_4 (the symmetric group in four objects). For example

$$\hat{Q}^{(12)}_{ijk\ell} = \hat{Q}_{jik\ell} \quad . \tag{16}$$

Now the symmetries of the array of two electron integrals can be written as

$$\hat{A}^{\tau} = \hat{A} \qquad \text{for} \qquad \tau \in \Gamma \tag{17}$$

where Γ is the subgroup of S_4 generated by $\{(12),\ (34),\ \ (13)(24)\ \}$.

In analogy to the use of triangular matrix $\underset{\sim}{L}$ in (6) for the conjugation of symmetric matrices, we decompose $\hat{A}$ as

$$\hat{A} = \sum_{\tau \in \Gamma} \hat{T}^{\tau} \tag{18}$$

uniquely by choosing so that $T_{ijk\ell} = 0$ if the indices i, j, k, ℓ are out of their standard canonical order [4]. Next it is noticed that

$$[\underset{\sim}{C}^t \otimes \underset{\sim}{C}^t \cdot \hat{T} \cdot \underset{\sim}{C} \otimes \underset{\sim}{C}]^{\tau} = \underset{\sim}{C}^t \otimes \underset{\sim}{C}^t \cdot \hat{T}^{\tau} \cdot \underset{\sim}{C} \otimes \underset{\sim}{C} \quad . \tag{19}$$

So if we set

$$\hat{B} = \underset{\sim}{C}^t \otimes \underset{\sim}{C}^t \cdot \hat{T} \cdot \underset{\sim}{C} \otimes \underset{\sim}{C} \tag{20}$$

then

$$\hat{Z} = \sum_{\tau} \hat{B}^{\tau} \quad . \tag{21}$$

The four successive summations are illustrated in Table 1. All of the final index symmetry is introduced by the sum over permutations at the end (21). This means, for instance, that $F_{ij\gamma\delta} \neq F_{ij\delta\gamma}$ for $\gamma \neq \delta$. Earlier introduction of some of the final index symmetry reduces the number of operations in steps 3 and 4. See specifically steps 3′ and 4′ in Table 1. Now.

$$\hat{Z} = \hat{V} + \hat{V}^{(12)} + \hat{V}^{(13)(24)} + \hat{V}^{(12)(13)(24)} \quad . \tag{22}$$

The grand total OpC comes out to be

$$\tfrac{1}{8} N^4M + \tfrac{1}{3} N^3M^2 + \tfrac{1}{4} N^2M^3 + \tfrac{1}{2} NM^4 \tag{23}$$

(ignoring terms of less than fifth order, i.e., $N, M \gg 1$).
This reduces to $29/24\ N^5 = 1.21\ N^5$ for $N = M \gg 1$ and $\frac{1}{8} N^4M$ for $N \gg M$.

Using only the simple symmetries $i \longleftrightarrow j, k \longleftrightarrow \ell$ in (12) yields $\frac{1}{4} N^4M + \frac{1}{2} N^3M^2 + \frac{1}{4} N^2M^3 + \frac{1}{2} NM^4$ which becomes $\frac{3}{2} N^5$ and $\frac{1}{4} N^4M$ for $N = M$ and $N \gg M$, respectively (see also Ref. [5]).

PROGRAMMING

Only the salient programming features will be presented here; a more detailed discussion, with program listings, is available upon request. A crucial restraint on machine calculations is array storage. The problem is especially acute for large molecular calculations, and in particular integral transformations of the type discussed herein. The method of full index symmetry presented above requires only a few of the incoming integrals ($\hat{T}$) at a time, in the normal canonical order. Each integral is used completely and not needed again. This means that the incoming integrals need not necessarily all be in core at once, and that the tape or disk on which they may reside need not be rewound or reread. Hence the number of incoming functions (N) is not limited by storage regiments.

The outgoing integrals ($\hat{Z}$), on the other hand must be referenced repeatedly. That they should all be in core at once is therefore a distinct advantage. This is feasible for approximately $M \leq 20$ with moderate sized cores (e.g., 40, 000 words). Larger sets might be handled using the integral sorting technique reported in Ref. [3], or dividing the transformation into disjoint spatial symmetry blocks [5], or as a last resort repeatative access of either the incoming [6] or outgoing [7] integrals.

The program we have in operation at Caltech has array storage requirements as shown in Table 2. The practical limits are approximately $N \leq 100$, $M \leq 20$. It is further possible to rearrange the loop structure within the program to capitalize on either zero transformation coefficients or zero incoming integrals, for an additional time savings.

SUMMARY AND CONCLUSIONS

We have seen that the retention of intermediate results, i.e., doing only one summation at a time, reduces the power dependence of the operation count for the transformation of two electron integrals from qN^8 to $q'N^5$. Further the use of index symmetry minimizes the multiplicative coefficient q'. The final formula, using the complete index symmetry is given by eq. (23). The limiting dominant terms are $29/24\ N^5$ and $\frac{1}{8}\ N^4M$ for $N = M \gg 1$ and $N \gg M$, respectively. Finally, the input and array storage requirements for the use of the complete index symmetry are no more restrictive than for previous N^5 methods [3, 5]. The application of index symmetry to the construction of mixed orbital/basis-function integrals for SCF calculations will be discussed in a following paper.

REFERENCES

[1] We will use the terms multiplication count and operation count interchangeably. Both are abbreviated by the symbol O C. By each operation we mean a multiplication with a subsequent addition. The compute time is presumed to be proportional to the O C.

[2] R. K. Nesbet, Rev. Mod. Phys. 35 (1963) 552.

[3] A. D. McLean, Proceedings of the Conference on Potential Energy Surfaces in Chemistry, Univ. of California, Santa Cruz, August, 1970, p. 87. Published as IBM Report RA 18, (1971).

[4] $i \geq j$, $k \geq \ell$, $ij \geq k\ell$.

[5] K. C. Tang and C. Edmiston, J. Chem. Phys. 52 (1970) 997.

[6] N. W. Winter has written and used such a program, private communication.

[7] W. T. Hunt, work in progress, private communication.

Table 1

Summary of operations by steps for the transformation of two electron integrals with full index symmetry.

Step	Summation	Approximate O_pC
1	$X_{ijk\delta} = \sum_{\substack{\ell=1 \\ k\ell \leq ij}}^{k} T_{ijk\ell} C_{\ell\delta}$	$\frac{1}{8} N^4 M$
2	$F_{ij\gamma\delta} = \sum_{k=1}^{i} X_{ijk\delta} C_{k\gamma}$	$\frac{1}{3} N^3 M^2$
3	$G_{i\beta\gamma\delta} = \sum_{j=1}^{i} F_{ij\gamma\delta} C_{j\beta}$	$\frac{1}{2} N^2 M^3$
4	$B_{\alpha\beta\gamma\delta} = \sum_{i=1}^{N} G_{i\beta\gamma\delta} C_{i\alpha}$	NM^4
3′	$Y_{i\beta\gamma\delta} = \sum_{j=1}^{i} [F_{ij\gamma\delta} + F_{ij\delta\gamma}] C_{j\beta}$	$\frac{1}{4} N^2 M^3$
4′	$V_{\alpha\beta\gamma\delta} = \sum_{i=1}^{N} Y_{i\beta\gamma\delta} C_{i\alpha}$	$\frac{1}{2} NM^4$

Table 2

Storage requirements for the transformation of two electron integrals with full index symmetry

Step	Array	Storage	For N = 60, M = 20
1	$\hat{T}$	$\frac{1}{2}$ N(N+1)	1, 830
	$\hat{C}$	NM	1, 200
	$\hat{X}$	NM	1, 200
2	$\hat{F}$	(use $\hat{T}$)	0
3′	$\hat{Y}$	$\frac{1}{2}$ M^2(M+1)	4, 200
4′	$\hat{Z}$	$\frac{1}{2}$ ms(ms+1)	22, 155
		[ms = $\frac{1}{2}$ M (M+1)]	30, 585

APPENDIX II

Index Symmetry and the Construction of Mixed-Orbital/Basis-Function Integrals

This Appendix discusses the general construction of mixed-orbital/basis-function integrals for use in Hartree-Fock and Generalized-Valence-Bond calculations. Also discussed is the construction of particle/hole integrals. Of special concern is the time savings available from the use of index symmetry.

INTRODUCTION

In the calculation of molecular wavefunctions by the Self-Consistent Field methods [such as Hartree-Fock (HF) and Generalized Valence Bond (GVB)], one must compute a variety of mixed orbital/basis-function integrals. The orbitals $\{\varphi_\alpha\}$ are linear combinations of the basis functions $\{\psi_i\}$, $\varphi_\alpha = \sum_i C_{i\alpha}\psi_i$. The necessary mixed integrals are among

$$\mathrm{AAMM}_{ij\gamma\delta} = \langle\psi_i\varphi_\gamma|1/r_{12}|\psi_j\varphi_\delta\rangle$$

$$= \int d^3x_1\ \psi_i(1)\psi_j(1)\ \int d^3x_2\ \frac{1}{r_{12}}\ \varphi_\gamma(2)\varphi_\delta(2)$$

$$\mathrm{AMAM}_{i\beta k\delta} = \langle\psi_i\varphi_\delta|\frac{1}{r_{12}}|\varphi_\beta\psi_k\rangle$$

$$= \langle\psi_i\psi_k|\frac{1}{r_{12}}|\varphi_\beta\varphi_\delta\rangle \qquad (1)$$

$$\mathrm{AMMM}_{i\beta\gamma\delta} = \langle\psi_i\varphi_\gamma|\frac{1}{r_{12}}|\varphi_\beta\varphi_\delta\rangle$$

and

$$\mathrm{MMMM}_{\alpha\beta\gamma\delta} = \langle\varphi_\alpha\varphi_r|\frac{1}{r_{12}}|\varphi_\beta\varphi_\delta\rangle\,.$$

For HF, only J- and K-like integrals are needed, i.e., $\mathrm{AAMM}_{ij\gamma\gamma}$ and $\mathrm{AMAM}_{i\beta k\beta}$. For non-orthogonal GVB, all are required.[1]

In the preceding Appendix (hereafter called I), the application of index symmetry to the transformation of two-electron integrals was discussed. It would be expected that index symmetry might be of importance in the construction of mixed-orbital/basis-function

integrals as well. As in I, a variety of schemes can be imagined. Once again we will evaluate the various techniques according to their multiplication counts,[2] (OpC), seeking to reduce both the order of basis-size dependence and the multiplicative coefficient.

AAMM and AMAM

The integrals in question are given by

$$AAMM_{ij\gamma\delta} = \sum_{K,\ell} AAAA_{ijk\ell}\, C_{k\gamma} C_{\ell\delta} \tag{2a}$$

$$AMAM_{i\beta k\delta} = \sum_{j,\ell} AAAA_{ijk\ell}\, C_{j\beta} C_{\ell\delta}. \tag{2b}$$

The construction of AMMM and MMMM from AAMM is simple:

$$\begin{aligned} AMMM_{i\beta\gamma\delta} &= \sum_{j} AAMM_{ij\gamma\delta}\, C_{j\beta} \\ MMMM_{\alpha\beta\gamma\delta} &= \sum_{i} AMMM_{i\beta\gamma\delta} C_{i\alpha} \end{aligned} \tag{3}$$

These two steps require only about $\frac{1}{2} N^2M^3$ and $\frac{1}{8} NM^4$ operations respectively and will be considered further below only for N =M.

A. Direct Multiplication: From I we expect that this technique will be inefficient, but we include it for completeness. The products $AAAA_{ijk\ell}C_{k\gamma}C_{\ell\delta}$ and $AAA_{ijk\ell}C_{i\beta}C_{\ell\delta}$ must be calculated. Even using index symmetry, this requires $\frac{1}{2}N^3(N+1)M(M+1) + N^3M(NM+1)$ multiplications, or about $3/2\ N^4M^2$ for $M \gg 1$. This can be reduced to N^4M^2 by saving $AAAA_{ijk\ell}C_{\ell\delta}$ and using it twice. The OpC becomes $2N^4$ for M = 1.

B. Density Matrices: As in paper I. we define the density matrices

$$D_{ij,\alpha\beta} = \begin{cases} [C_{i\alpha}C_{j\beta} + C_{i\beta}C_{j\alpha}] & i \neq j \\ C_{i\alpha}C_{j\beta} & i = j \end{cases} \qquad (4)$$

for all $i \geq j$, $\alpha \geq \beta$.

Then equation (2) becomes

$$AAMM_{ij\gamma\delta} = \sum_{k\ell=1}^{ns} AAAA_{ijk\ell}\, D_{k\ell,\gamma\delta} \qquad (5a)$$

$$AMAM_{i\beta k\delta} = \sum_{j=1}^{n} \sum_{\ell=1}^{n} AAAA_{ijk\ell}\, D_{j\ell,\beta\delta} \qquad (5b)$$

where $ns = \frac{1}{2}N(N+1)$, $ms = \frac{1}{2}M(M+1)$. The OpC then is $(ns)^2 ms + \frac{1}{2}N^3M(NM+1)$ or $(\frac{1}{8}+\frac{1}{2})N^4M^2 = \frac{5}{8}\,N^4M^2$ for $M \gg 1$ and $\frac{3}{4}\,N^4$ for $M = 1$. Some savings may be had by using more index symmetry in constructing AMAM, i.e.,

$$AMAM_{i\beta k\gamma} = \sum_{j\ell=1}^{ns} \{AAAA_{ijk\ell} + AAAA_{i\ell kj}\}\, D_{j\ell,\beta\delta} \qquad (5b')$$

for a total OpC of $\frac{3}{8}\,N^4M^2$ for $M \gg 1$ and $\frac{1}{2}\,N^4$ for $M = 1$. The use of density matrices saves a factor of 4 over direct multiplication, but does not change the order, which is 4 + 2 = 6.

C. Intermediate Matrices: As for the transformation of two-electron integrals in I, we save the intermediate result after the first summation, i.e.,

$$AAAM_{ijk\delta} = \sum_{\ell=1}^{N} AAAA_{ijk\ell}\, C_{\ell\delta} \cdot \tag{6}$$

This step takes $(ns)N^2M$ or $\frac{1}{2}N^4M$ multiplications. Then AAMM and AMAM are easily calculated

$$AAMM_{ij\gamma\delta} = \sum_{k=1}^{N} AAAM_{ijk\delta}\, C_{k\gamma} \tag{7a}$$

$$AMAM_{i\beta k\delta} = \sum_{\ell=1}^{N} AAAM_{ijk\delta}\, C_{j\beta} \tag{7b}$$

for $N(ns)(ms) \rightarrow \frac{1}{4} N^3M(M+1) \rightarrow \frac{1}{4} N^3M^2$ $M \gg 1$ and $\frac{1}{2} N^2M(NM+1) \rightarrow \frac{1}{2} N^3M^2$ multiplications respectively. The total OpC for equations (6) and (7) is then $\frac{1}{2} N^4M + \frac{3}{4} N^3M^2$ for $M \gg 1$. The approach of saving the intermediate matrix AAAM is therefore superior to that of density matrices for $M > 1$. We note that this technique lowers the order to $4 + 1 = 5$.

D. Index Symmetry: In I we found that the use of index symmetry reduced the multiplicative coefficient in the expression for the OpC. Such a savings is possible in the present case; it is not quite so large; and the procedure is quite a bit more complicated. The basic idea is

to consider transforming all the two-electron integrals from the basis set $\{\psi_i\}$ to a combined basis set $\{\psi_i, \varphi_\alpha\}$ or schematically A→ A + M. The kinds of integrals expected would be $(A+M)^4$ = AAAA, AMAM, AAMM, AMMM, MMMM, and others. For transformation, we would use the expanded N by (N+M) transformation matrix,

$$\underset{\sim}{E} = \left[\; \underset{\sim}{1} \;\middle|\; \underset{\sim}{C} \;\right] \quad N$$

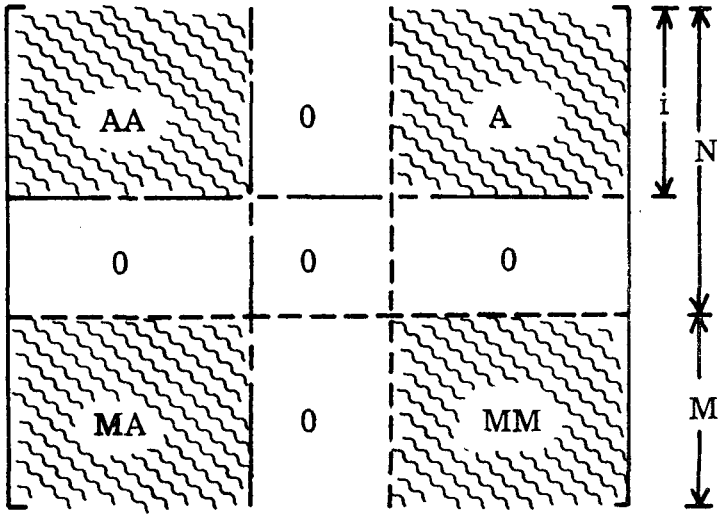
$$\leftarrow N \rightarrow \leftarrow M \rightarrow$$

This matrix is to be (symbolically) fed into a two-electron integral transformation program (i.e., the one discussed in I.). Each step of the transformation is to be analyzed, and superfluous operations eliminated.

1. First step: From I. we have

$$X_{ijkp} = \sum_{\substack{\ell=1 \\ k\ell \leq ij}}^{k} T_{ijk\ell}\, E_{\ell p}. \tag{8}$$

If we suppress the subscripts i and j for the moment, the k, p part of the $\hat{X}$ array can be represented by the matrix below.[3]



where

$$AA = \underline{AA} + (\underline{AA})^t, \quad AM = (MA)^t$$

$$AM_{k\delta} = \underline{AM}_{k\delta} + \underline{MA}_{k\delta} = \underline{AM}_{k\delta} + \sum_{\ell=k}^{i} \underline{AA}_{\ell k}\, C_{\ell\delta} \tag{12}$$

$$MM_{\gamma\delta} = \sum_{k=1}^{i} \{\underline{AM}_{kj}\, C_{k\gamma} + \underline{AM}_{kj}\, C_{k\delta}\} = \sum_{k=1}^{i} AM_{k\delta}\, C_{k\gamma}$$

$$= F_{ij\gamma\delta} + F_{ij\delta\gamma}.$$

3. Third Step: From I. we have

$$Y_{ipqr} = \sum_{j=1}^{i} [F_{ijqr} + F_{ijrq}]\, E_{jp}. \tag{13}$$

Even if the subscript i is understood we now run out of pictures, but we expect terms of the following types:

$$\underline{A}AA,\ \underline{A}AM,\ \underline{M}AA,\ \underline{A}MM,\ \underline{M}AM,\ \text{and}\ \underline{M}MM. \tag{14}$$

The terms AAA and MMM need not be calculated--they cannot be used in constructing AAMM and AMAM. The terms AAM and AMM involve no new work--they are just AM and MM of step two, i.e., $\underline{A}AM_{jk\delta} = \underline{A}M_{k\delta}(j)$ (the j was understood). This leaves MAA and MAM, which are given by

$$\underline{M}AA_{\beta k \ell} = \sum_{j=1}^{i} AA_{kl}(j)\, C_{j\beta}$$

$$\underline{M}AM_{\beta k\delta} = \sum_{j=1}^{i} AM_{k\delta}(j)\, C_{j\beta}. \qquad (15)$$

4. Fourth Step: The final step, which calculates only AAMM and AMAM comes from

$$Z_{pqrs} = \sum_{i=1}^{N} [Y_{iqrs}\, E_{ip} + Y_{iprs}\, E_{iq} + Y_{ispq}\, E_{ir} + Y_{irpq}\, E_{is}]. \qquad (16)$$

This becomes

$$AAMM_{ij\gamma\delta} = AMM_{j\gamma\delta}(i) + AMM_{i\gamma\delta}(j) + \sum_{t=i}^{N} \{MAA_{\delta ij}(t)\, C_{t\gamma} + MAA_{\gamma ij}(t)\, C_{t\delta}\} \qquad (17a)$$

$$AMAM_{i\beta k\delta} = \underline{M}AM_{\beta k\delta}(i) + \underline{M}AM_{\delta i\beta}(k) + \sum_{t=i,k}^{N} \{\underline{A}AM_{ik\delta}(t)\, C_{t\beta} + \underline{A}AM_{ki\beta}(t)\, C_{qs}\}. \qquad (17b)$$

It is to be remembered that

$$\underline{M}AM_{\delta p\beta}(q) = \underline{A}MM_{p\gamma\delta}(q) = 0 \text{ for } p > q. \tag{18}$$

5. Analysis: The OpC can be worked out by steps ($N \gg 1$), and is given in Table I. Including the calculation of AMMM and MMMM the OpC becomes (for $N, M \gg 1$).

$$\frac{3}{8}N^4M + N^3M^2 + \frac{1}{2}N^2M^3 + \frac{1}{8}NM^4. \tag{19}$$

It is informative to compare the OpC for the leading terms above ($\frac{3}{8}N^4M + N^3M^2$) with the corresponding OpC for the full transformation of two-electron integrals ($\frac{1}{8}N^4M + \frac{1}{3}N^3M^2$). The ratio of coefficients is exactly 3 to 1. This factor is explained by the fact that in transforming the two-electron integrals we form only one type of integral with three A's and one M, i.e., AAAM, while for orbital/basis-function integrals we need and form three of the possible four types, AAAM, AAMA, and AMAA, each at a cost of $\frac{1}{8}N^4M$. Hence there is a factor of three in the OpC. Each of the final integrals contains at least two M's. Any M put in the left-most location (MAAA) can always be chosen to be the second of the two M's (e.g., MAMA). This is why MAAA is not needed. There are three ways of putting on the second M for a factor of three in that step as well. With the intermediate matrix method, all four terms with only one M are needed, explaining the dependence of $\frac{1}{2}N^4M$. The second step is faster in the intermediate matrix method because the index symmetry that is used is introduced earlier.

This comparison with the OpC for just using intermediate matrices without using all the index symmetry is disheartening. For all that work we gain only 25% ($\frac{3}{8}N^4M$ vs. $\frac{1}{4}N^4M$) for $N \gg M$. Worse yet, for $M \rightarrow N$ we lose 10% (for the first two steps: $1\frac{3}{8}N^5$ vs. $1\frac{1}{4}N^5$, 7% overall: $2N^5$ vs. $1\frac{7}{8}N^5$). The two methods have the same OpC for $M = N/2$. Also if $M = N$ we should not do worse than just transforming to a new set of basis functions (as in I) with an OpC of $\frac{29}{24}N^5$. These difficulties are resolved by the following maneuver.

6. Change of Basis: We notice that any linearly independent combination of the old basis functions would be a suitable basis for the next SCF iteration. In specific, consider the set in which the last M functions are the old occupied orbitals and the first N-M functions are the old basis functions with the least overlap with the occupied orbitals. We call these the M's and Â's, respectively. The integrals needed are ÂÂMM, ÂMÂM, ÂMMM, and MMMM. As above, we consider transforming $A \rightarrow \hat{A} + M$ with the expanded transformation matrix.

$$\underset{\sim}{E} = \begin{bmatrix} \underset{\sim}{1} & \\ & \underset{\sim}{C} \\ \underset{\sim}{0} & \end{bmatrix} \begin{matrix} \uparrow \\ N-M \\ \updownarrow \\ M \\ \downarrow \end{matrix}$$

$$\overset{\longleftarrow N-M \longrightarrow}{\longleftarrow M \longrightarrow}$$

A similar procedure of symbolic transformation with the deletion of superfluous operations yields a method whose OpC reduces to $\frac{3}{8} N^4M$ for $N \gg M$ and $\frac{29}{24} N^5$ for $N = M$, and is always faster than any of the above discussed methods. Its derivation is, however, even more complicated and will not be reproduced here.

HARTREE-FOCK J AND K OPERATORS

For Hartree-Fock calculations one needs integrals of the form $AAMM_{ij\gamma\delta}$ and $AMAM_{i\gamma j\delta}$, but only for $\gamma = \delta$. The J and K operators are defined as

$$J^{\mu}_{pq} = \sum_{k=1}^{N} \sum_{\ell=1}^{N} AAAA_{pqk\ell}\, C^{\mu}_{k} C^{\mu}_{\ell}$$

$$K^{\mu}_{pq} = \sum_{j=1}^{N} \sum_{\ell=1}^{N} AAAA_{pjq\ell}\, C^{\mu}_{j} C^{\mu}_{\ell}. \tag{20}$$

A. Density Matrices: Defining the density matrices much as before

$$D^{\mu}_{k\ell} = (2-\delta_{k\ell})\, C^{\mu}_{k} C^{\mu}_{\ell}, \tag{21}$$

then

$$J^{\mu}_{pq} = \sum_{k\ell=1}^{ns} AAAA_{ijk\ell}\, D^{\mu}_{k\ell}$$

$$K^{\mu}_{pq} = \frac{1}{2} \sum_{j\ell=1}^{ns} [AAAA_{pjq\ell} + AAAA_{p\ell qi}] D^{\mu}_{j\ell} \tag{22}$$

and the OpC is $(\frac{1}{4} + \frac{1}{4})\, N^4M = \frac{1}{2}\, N^4M$. For closed shells we wish to calculate the sum

$$H_{pq} = \sum_{\mu} (2\, J^{\mu}_{pq} - K^{\mu}_{pq}). \tag{23}$$

To do this, we define a total density matrix

$$D_{pq} = \sum_{\mu} D^{\mu}_{pq}, \tag{24}$$

then[4]

$$H_{pq} = \sum_{k\ell=1}^{ns} [2\,(AAAA)_{pqk\ell} - \frac{1}{2}\,(AAAA)_{pkq\ell} - \frac{1}{2}\,(AAAA)_{p\ell qk}]D_{k\ell}. \tag{25}$$

So the total OpC is $\frac{1}{4}\,N^4$ for all closed shells and $\frac{1}{2}\,N^4M$ for the M open shells.

B. Index Symmetry for Open Shells: One cannot expect to compete with the OpC for the closed shell hamiltonian but some progress can be made on the open shells. By following the procedure of full index symmetry discussed above we merely apply the restriction that $\gamma = \delta$ (or $\beta = \delta$). This gives an OpC of $\frac{3}{8}\,N^4M + \frac{4}{3}\,N^3M$ or just $\frac{3}{8}\,N^4M$ if $N \gg 1$. This is a savings of 25% with only a slight increase in complexity, no extra work, almost no extra storage, and we need not symmetrize in integrals in advance (as for K above).

PARTICLE/HOLE INTEGRALS

In the Equations-of-Motion method of approximating molecular excited states certain occupied/virtual or particle/hole integrals are needed. In the special cases of the Tamm-Dancoff and Random-Phase Approximations[5] only the two-particle/two-hole integrals are needed. Higher approximations[6] require in addition the three-particle/one-hole and one-particle/three-hole integrals. Representing the particles by V and the holes by M, the necessary integrals are VVMM, VMVM, VMMM, and VVVM. We discuss below possible approaches for their construction.

A. VVVM and VMMM: The transformation to be accomplished is A→ V + M with superfluous operations eliminated. The need for both the VMMM and VVVM integrals reduces the amount of index symmetry which may be profitably used. The method of choice is then basically just that of intermediate-matrices. We let the smaller of the two sets (V and M) be represented by P(p functions), and the larger by Q (q functions). The flow chart of the transformation with the OpC for each step is shown in Figure 1. The total OpC is

$$\frac{1}{2}N^4p + \frac{1}{2}N^3p\,(q + \frac{1}{2}p) + N^2pq\,(q + \frac{1}{2}p) + Npq\,(\frac{1}{2}p^2 + \frac{1}{2}q^2 + \frac{3}{4}pq). \quad (26)$$

The special cases of $p = q = \frac{1}{2}N$ and $p = \frac{1}{4}N$, $q = \frac{3}{4}N$ give OpC's of $\frac{47}{64}N^5 = .734\ N^5$ and $\frac{495}{1024}N^5 = .48\ N^5$ respectively. As $p \to 0$, $q \to N$ the OpC decreases as $\frac{5}{2}N^4p$. This is to be compared with $\frac{29}{24}N^5 = 1.21\ N^5$ which would be necessary for the complete transformation of A → V + M as in I.

B. VVMM and VMVM: When only the VVMM and VMVM integrals are needed more of the index symmetry can be used (and hence time can be saved).

1. Intermediate Matrices: Figure 2 shows the flow chart for construction of VVMM and VMVM analogous to Fig. 1. This illustrates a method without using any additional index symmetry. The total OpC is

$$\frac{1}{2} N^4 p + \frac{1}{2} N^3 p \left(q + \frac{1}{2} p\right) + \frac{3}{2} N^2 p^2 q + \frac{3}{4} N p^2 q^2. \qquad (27)$$

This becomes $\frac{43}{64} N^5 = .672\ N^5$ and $\frac{303}{1024} N^5 = .296\ N^5$ for $p = q = \frac{1}{2} N$ and $p = \frac{1}{4} N$, $q = \frac{3}{4} N$ respectively. As $p \to 0$, $q \to N$ that OpC decreases as $N^4 p$.

2. Index Symmetry: The technique is to transform to AAPP and APAP with full index symmetry as above. This has an OpC of $\frac{3}{8} N^4 p + N^3 p^2$. The final transformation to QQPP and QPQP gives the OpC of $\frac{3}{4} N^2 p^2 q + \frac{3}{2} N p^2 q^2$. The grand total OpC is

$$\frac{3}{8} N^4 p + N^3 p^2 + \frac{3}{4} N^2 p^2 q + \frac{3}{2} N p^2 q^2. \qquad (28)$$

This reduces to $\frac{5}{8} N^5 = .625\ N^5$ and $\frac{125}{512} N^5 = .244\ N^5$ for $p = q = \frac{1}{2} N$ and $p = \frac{1}{4} N$, $p = \frac{3}{4} N$, respectively. A $p \to 0$, $q \to N$, the OpC decreases as $\frac{3}{8} N^4 p$.

PROGRAMMING

As could be expected the cases which have the largest OpC's also have the largest storage requirements, due to the large number of basis functions. The two aspects must be considered together, especially since a faster, more complicated approach may require more storage. But when the basis set is so large that neither the incoming integrals nor the outgoing integrals can be all in core at once, repetitive processing of some kind must be used, and the specific storage requirements of the transformation scheme become less important. See also the comments in I.

We consider here the case of construction of AAMM and AMAM with full index symmetry. This transformation can conveniently be arranged to capitalize on zero-coefficients, zero-integrals, or spatial symmetry. The program structure is simplest if the incoming integrals are in canonical order and all the outgoing integrals are in core. The storage for such a program is shown in Table II. The example of N = 24, M = 6 will fit in a moderate sized core (40,000 words). This example is larger than any case for which the method has been used, since for this many basis functions and non-orthogonal orbitals the rest of the GVB calculation becomes very expensive. In any case we see that the scratch space needed (AA, AAM, and MAA in Table II) accounts for only 22% of the total storage

requirement. For open-shell Hartree-Fock we may use the same table, just set ms = M, and forget AMMM and MMMM. The practical limits are then about N = 30, M = 12 (open-shell orbitals). The method is essentially unlimited if each open-shell orbital is handled individually.

SUMMARY

We have found through the use of intermediate matrices and the maximum use of index symmetry, what appear to be the fastest techniques for the construction of mixed orbital/basis-function integrals. A crucial aspect of transformations with index symmetry is that the intermediate results need not have the correct final index symmetry.

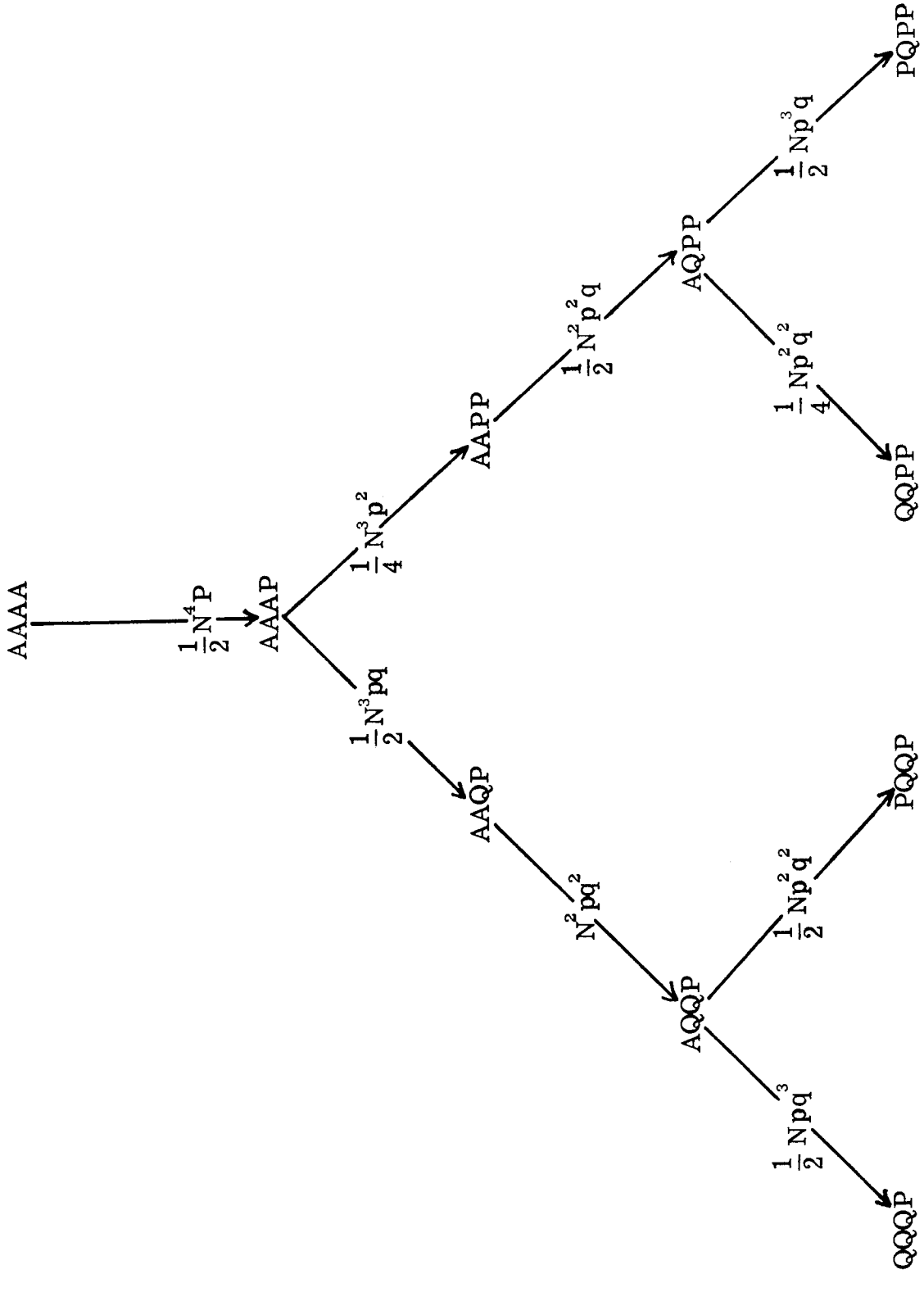


Fig. 1. Flow chart for the construction of VVVM, VVMM, VMVM, and VMMM particle/hole integrals.

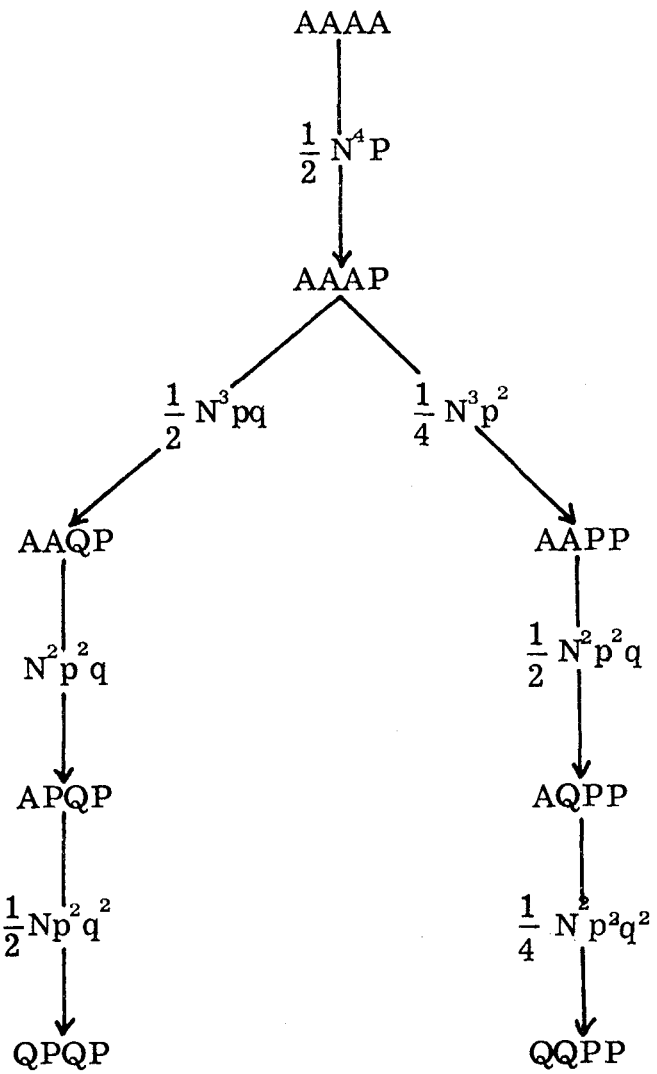


Fig. 2. Flow chart for the construction of VVMM and VMVM particle/hole integrals.

Table I. Summary of operations by steps for the construction of orbital/basis-function integrals using full index symmetry.

Step	To Construct	Approximate OpC
1	$\underline{AM}$	$\frac{1}{8}N^4M$
2	$\underline{MA}$ (or AM)	$\frac{1}{8}N^4M$
	MM	$\frac{1}{6}N^3M(M+1)$
3	$\underline{M}AA$	$\frac{1}{8}N^4M$
	$\underline{M}AM$	$\frac{1}{3}N^3M^2$
4	AMAM	$\frac{1}{3}N^3M^2$
	AAMM	$\frac{1}{6}N^3M(M+1)$

Table II. Storage requirements for the construction of AAMM, AMAM, AMMM, MMMM with full index symmetry.

Array	Storage	for N = 24, M = 6
C	NM	144
$\underline{AA}$	$\frac{1}{2}N(N+1) = ns$[a]	300
$\underline{A}AM$	N^2M	3456
$\underline{M}AA$	(ns)M	1800
AAMM	(ns)(ms)	6300
AMAM	$\frac{1}{2}NM(NM+1)$	10440
AMMM	NM(ms)	3024
MMMM	$\frac{1}{2}(ms)(ms+1)$	231
		25695

[a] $ns = \frac{1}{2}N(N+1)$, $ms = \frac{1}{2}M(M+1)$.

REFERENCES

1. W. A. Goddard III, Phys. Rev. 157, 81 (1967).
2. As in I. we will use the terms multiplication count and operation count interchangeably, both are abbreviated as OpC. By each operation we mean a multiplication with a subsequent addition.
3. A symbol representing an array of integrals in which one or more of the characters is underlined, has been summed or is nonzero only for indices in a restricted order. For example, in

$$\underline{AAAM}_{ijk\delta} = \underline{AM}_{k\delta} = \sum_{\ell=1}^{k} \underline{AA}_{k\ell}\, C_{\ell\delta} = \sum_{\ell=1}^{k} \underline{AAAA}_{ijk\ell}\, C_{\ell\delta}.$$

The summation over ℓ is limited by k (also $k\ell \leq ij$), further $j \leq i$. Whereas

$$\underline{AAAM}_{ijk\delta} = AM_{k\delta} = \sum_{\ell=1}^{k} \underline{AA}_{k\ell}\, C_{\ell\delta} + \sum_{\ell=k+1}^{i} \underline{AA}_{\ell k}\, C_{\ell\delta}$$

has had the indices for the last two positions (k, ℓ) summed or non-zero to the same limit ($k \leq i$, $\ell \leq i$). The restriction $i \geq j$ and $i \geq k$ still applies. Canonical order ($i \geq j$, $k \geq \ell$, $ij \geq k\ell$) is followed throughout.

$$\underline{AAAA}_{ijk\ell} = AAAA_{ijk\ell}\,(1 - \tfrac{1}{2}\delta_{i,j})(1 - \tfrac{1}{2}\delta_{k,\ell})(1 - \tfrac{1}{2}\delta_{k\ell,ij})$$

$$i \geq j,\ k \geq \ell,\ ij \geq k\ell.$$

4. See, for example, C. C. J. Roothaan and P. S. Bagus, Methods in Computational Physics (Academic Press, New York, 1963), Vol. 2.

5. T. H. Dunning, Jr., and V. McKoy, J. Chem. Phys., 47, 1735 (1967).

6. J. Rose, T. Shibuya, and V. McKoy, J. Chem. Phys., in press.

APPENDIX III.

Supermatrix Methods for Pedestrians

A. The Variational Condition-Iterative Solution: The most basic tool in bound state molecular quantum mechanics is the Rayleigh-Ritz-Schrödinger variational principle.[1] The principal states that a parameterized approximate wavefunction, $\Psi(\lambda_1, \lambda_2, \cdots)$, may be optimized with respect to these parameters by requiring that the average energy, $E = \langle \Psi | \mathcal{H} | \Psi \rangle / \langle \Psi | \Psi \rangle$, be stationary with respect to variation of these parameters, i.e., $\partial E / \partial \lambda_i = 0$.

The kind of approximate wavefunction we have in mind is a projected orbital product, $P\Phi = P\varphi_1 \varphi_2 \cdots \varphi_n$, the parameters are the linear coefficients describing the orbitals in terms of the basis functions, $\varphi_k = \sum_\alpha C_k^\alpha \eta_\beta$. The variational condition then becomes

$$\frac{\partial E}{\partial C_k^\alpha} = \frac{\partial}{\partial C_k^\alpha} \frac{\langle \Phi | \mathcal{H} P | \Phi \rangle}{\langle \Phi | P | \Phi \rangle} = 2\mathrm{Re} \frac{\langle \Phi_k^\alpha | (\mathcal{H} - E) P | \Phi \rangle}{\langle \Phi | P | \Phi \rangle} = 0 , \qquad (1)$$

where Φ_k^α is the original orbital product with orbital φ_k replaced by basis function η_α. For real orbitals, this is rewritten as

$$\langle \Phi_k^\alpha | (\mathcal{H} - E) P | \Phi \rangle = 0 . \qquad (1')$$

Equation (1′) is to be solved iteratively. A trial set of orbitals, $\Phi^{(0)}$, is selected and from them, and somehow using Eq. (1′), a new set $\Phi^{(1)}$ is found. The process is to be continued until the orbitals no longer change, i.e., until (1′) is satisfied. This Appendix discusses some recent developments on the two basic techniques of iteration: The

hamiltonian-matrix and the super-matrix methods.

B. The Hamiltonian-Matrix: The essence of the hamiltonian method is selection of an eigenvalue equation for each orbital based on the factorization of Eq. (1′), such as $\langle \Phi_k^\alpha | (\mathcal{H} - E)P | \Phi \rangle = \sum_\beta \langle \Phi_k^\alpha | (\mathcal{H} - E)P | \Phi_k^\beta \rangle C_k^\beta$. Three such methods will be mentioned here.

1. Constrained Variation[2, 3]: While solving for the optimum orbitals, we know certain relations that the final orbitals will satisfy. These relations include normalization of the orbitals, and perhaps mutual orthogonality (as in Hartree-Fock). These relations can be ensured throughout the iteration scheme by the method of Lagrange multipliers (or orbital energies). The idea is to consider variations of a modified functional, such as

$$I = E - \sum_k \epsilon_k'' [\langle \varphi_k | \varphi_k \rangle - 1] \quad . \tag{2}$$

It is important to note that due to the Lagrange constraint terms, $\epsilon_k'' [\langle \varphi_k | \varphi_k \rangle - 1]$ in Eq. (2), we are free to choose $\langle \varphi_k | \varphi_k \rangle = 1$ in any expression in which it occurs. It is not to be varied in the differentiation

$$\frac{\partial I}{\partial C_k^\alpha} = \frac{\partial E}{\partial C_k^\alpha} - \epsilon_k'' \frac{\partial \langle \varphi_k | \varphi_k \rangle}{\partial C_k^\alpha} = 0 \tag{3}$$

except within the constraint term itself. Equation (3) can now be written as

$$\sum_\beta \langle \Phi_k^\alpha | (\mathcal{H} - E)P | \Phi_k^\beta \rangle^\perp C_k^\beta = \sum_\gamma \epsilon_k' \langle \eta_\alpha | \eta_\gamma \rangle C_k^\gamma \tag{4}$$

or

$$H_k^{\perp} \varphi_k = \epsilon_k' S \varphi_k \ , \tag{5}$$

where $(H_k^{\perp})_{\alpha\beta} = \langle \Phi_k^{\alpha} | (\mathcal{H} - E)P | \Phi_k^{\beta} \rangle^{\perp}$, $S_{\alpha\beta} = \langle \eta_\alpha | \eta_\beta \rangle$. The superscript $\perp$ indicates that all the constraints are satisfied and were not varied. As an example, consider the case of two-electron singlet G1. Then (as in Ref. 4) $P = \frac{1}{2}[1 + (12)]$ and

$$\begin{aligned}(H_2^{\perp})_{\alpha\beta} = \tfrac{1}{2}\{ &\langle \eta_\alpha | h | \eta_\beta \rangle + \langle \eta_\alpha | h | \varphi_1 \rangle \langle \varphi_1 | \eta_\beta \rangle + \langle \eta_\alpha | \varphi_1 \rangle \langle \varphi_1 | h | \eta_\beta \rangle \\ &+ \langle \eta_\alpha \varphi_1 | 1/r_{12} | \eta_\beta \varphi_1 \rangle + \langle \eta_\alpha \varphi_1 | 1/r_{12} | \varphi_1 \eta_\beta \rangle \\ &- E \langle \eta_\alpha | \varphi_1 \rangle \langle \varphi_1 | \eta_\beta \rangle \} \ .\end{aligned} \tag{6}$$

The iterative scheme proceeds simply as follows:

a) choose the initial orbitals $[\varphi_k^{(0)}]$

b) construct the effective hamiltonian for each orbital $[H_k^{(\nu)}]$

c) diagonalize to find the new orbitals
$[H_k^{(\nu)} \varphi_k^{(\nu+1)} = \epsilon_k'^{(\nu+1)} S \varphi_k^{(\nu+1)}]$

d) unless converged, go back to step (b).

The technique converges rather quickly for Hartree-Fock, and quite slowly for GI.

2. Unconstrained Variation[5, 6]: For awhile it was thought that the convergence of the GI equations could be accelerated by an iteration scheme based directly on Eq. (1′). The orbital hamiltonian was to be given by

$$(H_k^0)_{\alpha\beta} = \langle \Phi_k^{\alpha} | (\mathcal{H} - E)P | \Phi_k^{\beta} \rangle \ , \tag{7}$$

with the self-variation terms retained (this is the same as not using orbital energies). The eigenvalue equation would then be something like

$$H_k^0 \varphi_k = \beta_k \varphi_k \ . \tag{8}$$

The eigenvalue β_k would be the change in the orbital energy [ϵ_k' of Eq. (5)] from one iteration to the next. At convergence $\beta_k = 0$.

For the two-electron singlet G1 example as above, the hamiltonian for orbital φ_2 is

$$\begin{aligned}(H_2^0)_{\alpha\beta} = \tfrac{1}{2}\{ &\langle \eta_\alpha | h | \eta_\beta \rangle \langle \varphi_1 | \varphi_1 \rangle + \langle \eta_\alpha | h | \varphi_1 \rangle \langle \varphi_1 | \eta_\beta \rangle \\ &+ \langle \eta_\alpha | \varphi_1 \rangle \langle \varphi_1 | h | \eta_\beta \rangle + \langle \eta_\alpha | \eta_\beta \rangle \langle \varphi_1 | h | \varphi_1 \rangle \\ &+ \langle \eta_\alpha \varphi_1 | 1/r_{12} | \eta_\beta \varphi_1 \rangle + \langle \eta_\alpha \varphi_1 | 1/r_{12} | \varphi_1 \eta_\beta \rangle \\ &- E[\langle \eta_\alpha | \varphi_1 \rangle \langle \varphi_1 | \eta_\beta \rangle + \langle \eta_\alpha | \eta_\beta \rangle \langle \varphi_1 | \varphi_1 \rangle] \} \ .\end{aligned}$$

The convergence of this method turned out to be even worse.

3. The Hamiltonian-Virtual-Metric[6]: This highly successful method gives not only rapid convergence but also a rigorous interpretation for virtuals and excited states. The hamiltonian is based once again on Eq. (1′) with self-variation terms retained. But Eq. (1′) is first partitioned in a special way

$$\sum_\beta \langle \Phi_k^\alpha | \mathcal{H} P | \Phi_k^\beta \rangle C_k^\beta = E \sum_\gamma \langle \Phi_k^\alpha | P | \Phi_k^\gamma \rangle C_k^\gamma \ . \tag{9}$$

Now Eq. (9) is to be solved directly for $\{C_k^\gamma\}$ with the total energy E as the eigenvalue. This can be rewritten as

$$(H_k^v)_{\alpha\beta} = \langle \Phi_k^\alpha | \mathcal{H}P | \Phi_k^\beta \rangle \tag{10a}$$

$$(M_k)_{\alpha\beta} = \langle \Phi_k^\alpha | P | \Phi_k^\beta \rangle \tag{10b}$$

$$H_k^v \varphi_k = E\, M_k \varphi_k \quad . \tag{10c}$$

The hamiltonian for orbital φ_k, H_k^v, and the corresponding metric M_k does not depend on the orbital φ_k itself, only on the other orbitals, φ_ℓ, $\ell \neq k$. This means that each solution to Eq. (10c) [i.e., φ_k and the virtuals] is a variationally optimum orbital with the restriction that the other orbitals remain frozen. This is why the convergence is good. The conclusions that result about excited states and upper bounds are presented somewhat later below.

The solution to Eq. (10c) proceeds by the standard techniques [notice the formal similarity to Eq. (5)]. One finds a matrix W_k such that $W_k^t M_k W_k = 1$, then $W_k^t H_k^v W_k$ is diagonalized to find the eigenvalues and eigenvectors. An exception to this procedure, and an important aspect of this Hamiltonian-Virtual-Metric (HVM) method, is that orthogonalities and orbital restrictions due to the projection operator (P) are automatically guaranteed by the metric on the right-hand side of Eq. (10c).

To see what happens we examine the case of a two-electron triplet,

$$\begin{aligned} H_2^v &= \tfrac{1}{2}\{h\langle\varphi_1|\varphi_1\rangle + \langle\varphi_1|h|\varphi_1\rangle - |\varphi_1\rangle\langle\varphi_1|h| - h|\varphi_1\rangle\langle\varphi_1| + J_1 - K_1\} \\ M_2 &= \tfrac{1}{2}\{\langle\varphi_1|\varphi_1\rangle - |\varphi_1\rangle\langle\varphi_1|\} \quad . \end{aligned} \tag{11}$$

From this we notice

$$H_2^V \varphi_1 = M_2 \varphi_1 = 0. \tag{12}$$

This means that M is singular and that no matrix W can be found such that $W^tMW=1$ as was required. So instead we find a new matrix U such that $U^tM_2U = 1 - |\varphi_1\rangle\langle\varphi_1|$ (M is already in this form for the simple two-electron example above). Then we find the eigenvectors and eigenvalues from U^tH^VU. The solutions will already be orthogonal to φ_1 since the operator U projects onto the space orthogonal to φ_1. This orthogonality is just what was required for a triplet.

C. The Supermatrix[6, 8]: One may consider Eq. (1′) directly as a system of nonlinear equations[9] for the coefficients. This is the motivation of the modified Newton-Raphson or supermatrix method.

1. Formalism: The collection of coefficients are to be assembled into one column vector, called the coefficient-supervector[10]

$$\Theta = \begin{bmatrix} C_1^1 \\ \cdot \\ \cdot \\ \cdot \\ C_1^m \\ C_2^1 \\ \cdot \\ \cdot \\ \cdot \\ C_n^m \end{bmatrix} \tag{13}$$

A supervector consisting of a single orbital is written as

$$ {}^{i}\Theta = \begin{bmatrix} 0 \\ \cdot \\ \cdot \\ 0 \\ \varphi_i \\ 0 \\ \cdot \\ , \\ 0 \end{bmatrix} \tag{14} $$

We sometimes refer to an element of a supervector as $\Theta_{i\mu} = C_i^{\mu}$ and sometimes as Θ_k. When only one subscript appears, it may be thought of as a supersubscript, a combination of the orbital-index (i) and the basis function-index (μ) for which it stands.

We now rewrite Eq. (1) as

$$ X_{i\mu} = \frac{\partial E}{\partial C_i^{\mu}} = 2\mathrm{Re}\, \frac{\langle \Phi_i^{\mu} | (\mathcal{H} - E)P | \Phi \rangle}{\langle \Phi | P | \Phi \rangle} = 0 \, . \tag{15} $$

The supermatrix is defined by

$$ B_{ij} = \frac{\partial X_i}{\partial \Theta_j} = \frac{\partial X_j}{\partial \Theta_i} \tag{16a} $$

or

$$ B_{i\mu,k\alpha} = \frac{\partial^2 E}{\partial C_i^{\mu} \partial C_k^{\alpha}} \tag{16b} $$

$$ = \frac{2}{\langle \Phi | P\Phi \rangle} \mathrm{Re} \{ \langle \Phi_i^{\mu} | Op | \Phi_k^{\alpha} \rangle + \langle \Phi_{ik}^{\mu\alpha} | Op | \Phi \rangle (1 - \delta_{ik}) $$

$$ - \frac{2}{\langle \Phi | P | \Phi \rangle} [\langle \Phi_i^{\mu} | P | \Phi \rangle \mathrm{Re} \langle \Phi_k^{\alpha} | Op | \Phi \rangle $$

$$ + \langle \Phi_k^{\alpha} | P | \Phi \rangle \mathrm{Re} \langle \Phi_i^{\mu} | Op | \Phi \rangle] \} , $$

where $Op = (\mathcal{H} - E)P$ and $\Phi_{ik}^{\mu\alpha}$ is Φ with orbitals φ_i and φ_k both removed and replaced by basis functions η_μ and η_α, respectively. In most work, B and X are multiplied by the inconsequential factor $\langle \Phi | P | \Phi \rangle / 2$. Further, in some discussions and in some computer programs, only the $\langle \Phi_i^\mu | Op | \Phi_k^\alpha \rangle$ and $\langle \Phi_{ik}^{\mu\alpha} | Op | \Phi \rangle (1 - \delta_{ij})$ terms are included in B.

The solution to Eq. (15) and hence the determination of the optimum orbitals proceeds as follows:

a) choose the initial orbitals $[\Theta^\nu]$

b) construct the supermatrix, B^ν, and the error vector, X^ν

c) the new orbitals satisfy the equation, [6, 8]

$$B^\nu \delta = B^\nu [\Theta^{\nu+1} - \Theta^\nu] = -X^\nu \tag{17a}$$

so that formally

$$\Theta^{\nu+1} = \Theta^\nu + \delta = \Theta^\nu - [B^\nu]^{-1} X^\nu \tag{17b}$$

d) unless converged ($|\delta| = |X| = 0$), go back to step (b).

This technique is found to work fantastically well. The method converges quadratically [$|\delta^{\nu+1}| = |\delta^\nu|^2$, if it converges at all]. There is one important but soluble difficulty. Equation (17b) requires the inversion of the supermatrix; it is found that near convergence B is singular; that is, the inverse does not exist.

2. Zeros: As mentioned above in Sec. B. 1., there are a number of relations that the orbitals may be chosen to obey, such as normalization and perhaps mutual orthogonality. We notice in specific that the average energy is independent of the normalization of each of the orbitals. So that all derivatives of the energy with respect to the normalization

vanish. Hence the B-matrix, which is the matrix of second derivatives, has a zero eigenvalue, and is therefore singular.

Now while iterating with the supermatrix method we recognize that there are certain types of changes in the orbitals that we do not want to make, i.e., those changes that do not affect the energy. For the example of the two-electron triplet, there are four such changes:

a) adding $\lambda\varphi_1$ to φ_1 (renormalization),

$$\begin{bmatrix} \varphi_1 \\ \varphi_2 \end{bmatrix} + \lambda \begin{bmatrix} \varphi_1 \\ 0 \end{bmatrix} \tag{18a}$$

b) adding $\lambda\varphi_2$ to φ_2 (again renormalization)

$$\begin{bmatrix} \varphi_1 \\ \varphi_2 \end{bmatrix} + \lambda \begin{bmatrix} 0 \\ \varphi_2 \end{bmatrix} \tag{18b}$$

c) adding $\lambda\varphi_2$ to φ_1 (exchange)

$$\begin{bmatrix} \varphi_1 \\ \varphi_2 \end{bmatrix} + \lambda \begin{bmatrix} \varphi_2 \\ 0 \end{bmatrix} \tag{18c}$$

d) finally, adding $\lambda\varphi_1$ to φ_2

$$\begin{bmatrix} \varphi_1 \\ \varphi_2 \end{bmatrix} + \lambda \begin{bmatrix} 0 \\ \varphi_1 \end{bmatrix} \tag{18d}$$

The space spanned by these irrelevant change vectors is called the space of invariants. As the iteration scheme converges, there will be several eigenvalues (four in the above case) of the supermatrix that become very small. Each of these vanishing eigenvalues is called a zero. There is one for each way of changing the orbitals without changing the energy. A summary of the situation for a few simple cases is presented in Table I.

TABLE I. Zeros of the Supermatrix.

NX	Spin	P	No. of zeros	Type[a]
2	0	G1	2	N
2	1	G1	4	N, E
3	1/2	G1 or SOGI	3	N
3	1/2	GF	5	N, E
3	3/2	G1	9	N, E
4	0	G1 or SOGI	4	N
4	0	GF	8	N, E
4	1	G1	6	N, E
4	1	GF	10	N, E
4	1	SOGI	4	N
5	1/2	G1 or SOGI	5	N
2	0	$^1\Sigma_g^+$	3	N, R
2	1	$^3\Sigma_g^+$	7	N, E, R
2	0, 1	$^{1,3}\Sigma_u^+$	5	N, E, R
2	0, 1	$^{1,3}\Pi_{g,u}$	9	N, E, R

[a] N = normalization, E = exchange, R = reflection.

The general rule for counting the number of zeros is to take the sum of the squares of the numbers of electrons antisymmetrically coupled together. Thus, for four-electron triplet GF we get $3^2 + 1 = 10$, as in Table I.

3. Projection: The solution to the problem of the nearly-zero eigenvalues and singularity of B is to project the problem [Eqs. (17a) and (17b)] out of the space of invariants. For this there are two techniques at present.

a) Explicit projection: For simple cases, all the vectors in the space of invariants can be identified as combinations of the orbitals (or, in the case of spatial projection, as pieces of the orbitals). A resolution of the singularity of the B matrix can then be obtained by explicitly projecting that matrix onto the subspace of all possible variations orthogonal to the space of invariants, or simply said, projecting out the unwanted variations. Suppose $\{\xi_i\}_{i=1}^{q}$ is an orthonormal basis for the space of invariants constructed from the (current, not necessarily converged) orbitals. If we define

$$R = \prod_{i=1}^{q} (1 - |\xi_i\rangle\langle\xi_i|) \tag{19a}$$

and

$$B' = RBR , \quad X' = RX . \tag{19b}$$

Then

$$B'\delta = -X' \tag{19c}$$

can be solved for the changes desired.

When B′ is diagonalized we will get q exactly zero eigenvalues. The corresponding eigenvectors are the ξ_i's (or linear combinations of them). We then may follow the technique of deleting the "zeros"; they have the desirable quality of being exactly zero and are therefore identifiable. This procedure seems to work very well and the SCF almost

always converges. Since the zeros are zero, we could even use the faster technique of Gaussian elimination with maximal pivots. When the largest pivot is zero, we just forget the rest of the matrix, since it must all be in the space of invariants.

b) Implicit projection: Levin[11] and Goddard [8] discovered that the matrix

$$A_{i\alpha,\, i\beta} \equiv \langle \Phi_i^{\alpha} | P | \Phi_j^{\beta} \rangle \tag{20}$$

has as its null space exactly the space of invariants as constructed from the current orbitals, less the current coefficient supervector itself. Consider the previous example of a two-electron triplet,

$$A \cdot \begin{bmatrix} 0 \\ \varphi_1 \end{bmatrix} = \begin{bmatrix} \langle \Phi_1' | P | \varphi_1 \varphi_1 \rangle \\ \langle \Phi_2' | P | \varphi_1 \varphi_1 \rangle \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$A \cdot \begin{bmatrix} \varphi_2 \\ 0 \end{bmatrix} = \begin{bmatrix} \langle \Phi_1' | P | \varphi_2 \varphi_2 \rangle \\ \langle \Phi_2' | P | \varphi_2 \varphi_2 \rangle \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \tag{21}$$

$$A \cdot \begin{bmatrix} \varphi_1 \\ -\varphi_2 \end{bmatrix} = \begin{bmatrix} \langle \Phi_1' | P | \varphi_1 \varphi_2 \rangle - \langle \Phi_1' | P | \varphi_1 \varphi_2 \rangle \\ \langle \Phi_2' | P | \varphi_1 \varphi_2 \rangle - \langle \Phi_2' | P | \varphi_1 \varphi_2 \rangle \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

so the diagonalization of A is a way of finding the space of invariants, and the eigenvectors can be used to transform B as was done above.

D. Excited States: The principal difficulty in solving for excited state wavefunctions is not getting the wavefunction but rather showing that it approximates the excited state one had in mind. To do this we need an upper bound principle.

1. Upper bounds - HVM: For wavefunctions constructed from configuration interaction (CI) the variational principle itself provides the rule that the k^{th} eigenvalue is an upper bound to the k^{th} state. For orbital product wavefunctions the situation is usually much more complicated. The HVM method provides a clear upper bound rule based itself on an interaction of configurations.

Suppose we have converged to a set of orbitals with each orbital the lowest solution of its own HVM equation, except the last orbital (φ_n), which is the k^{th} solution. Now consider a CI on all configurations of the form $\varphi_n^{(j)}\Phi_n'$ (i.e., $\varphi_n^{(j)}$, the j^{th} eigenfunction of H_n^v, replaces $\varphi_n^{(k)}$). The CI hamiltonian is

$$\begin{aligned} \mathcal{H}_{j\ell} &= \langle \varphi_n^{(j)}\Phi_n' | \mathcal{H}\mathbf{P} | \varphi_n^{(\ell)}\Phi_n' \rangle \\ &= \langle \varphi_n^{(j)} | H_n^v | \varphi_n^{(\ell)} \rangle \ , \end{aligned} \tag{22a}$$

and the CI overlap matrix is

$$\mathcal{S}_{j\ell} = \langle \varphi_n^{(j)}\Phi_n' | \mathbf{P} | \varphi_n^{(\ell)}\Phi_n' \rangle = \langle \varphi_n^{(j)} | M_n | \varphi_n^{(\ell)} \rangle \ , \tag{22b}$$

but now comparison with Eq. (10c) and a little manipulation gives

$$\mathcal{H}_{j\ell} = E^{(j)}\mathcal{S}_{jj}\delta_{k\ell} \ . \tag{23}$$

The CI problem is already diagonal, with the same eigenvalues as Eq. (10c). This gives the important result that the energies $E^{(j)}$ are rigorous upper bounds: $E^{(j)} \geq E_{exact}$ for the j^{th} state.

2. Supermatrix eigenvalues - the ground state: The eigenvalues of the supermatrix at convergence also give information about the

wavefunction. First, consider the following theorem from Fleming.[12] Given a twice differentiable function of n variables

$$f(x) = f(x_1, x_2, x_3, \cdots, x_n),$$

Then we define

$$\underset{\sim}{\nabla} f(x^0) \equiv \left(\frac{\partial f}{\partial x_1}, \frac{\partial f}{\partial x_2}, \cdots, \frac{\partial f}{\partial x_n}\right)_{x=x^0}$$

$$\hat{Q}: f(x^0) \equiv \left[\begin{array}{ccc} \frac{\partial^2 f}{\partial x_1^2} & \frac{\partial^2 f}{\partial x_1 \partial x_2} & \cdots \frac{\partial^2 f}{\partial x_1 \partial x_n} \\ & & \\ \frac{\partial^2 f}{\partial x_n \partial x_1} & & \frac{\partial^2 f}{\partial x_n^2} \end{array}\right]_{x = x^0}$$

Note that $\underset{\sim}{\nabla}$ produces a vector, $\hat{Q}$ a matrix.

<u>Theorem:</u> suppose $\underset{\sim}{\nabla} f(x^0) = 0$, then

$\hat{Q}: f(x^0)$ is positive semi-definite

implies that f has a relative minimum at x^0

$\hat{Q}: f(x^0)$ is negative semi-definite

implies a relative maximum at x^0

$\hat{Q}: f(x^0)$ is positive (negative) definite

implies a strict relative minimum (maximum) at x^0

$\hat{Q}: f(x^0)$ is indefinite

implies that x^0 is a saddle point.

Now consider the case when

$$f = E(\Theta) \quad \text{the energy}$$

$$\underset{\frown}{\nabla} f = X(\Theta) \quad \text{the X vector}$$

$$\hat{Q} : f = B(\Theta) \quad \text{the supermatrix.}$$

For the ground state of the system we know independently that E is a relative minimum. Hence B must have no negative eigenvalues. So if the supermatrix approach converged with one or more negative eigenvalues, we know that it did not convert to the lowest energy solution of that symmetry.

3. Excited states and the supermatrix: Having found in the previous section that the B matrix should have no negative eigenvalues, and viewing the eigenvectors as the various ways of changing the orbitals, we might hope that for excited states the number of negative eigenvalues would be equal to the number of lower states. This would make sense since the only way to lower the energy of a converged excited state is to add a piece of a lower state. Unfortunately a rigorous demonstration of the principle does not, at the moment, exist, but the usefulness and plausibility of the idea will be illustrated below.

Suppose we have converged an excited state wavefunction as before with all the orbitals the lowest solution of their own HVM equation, except the last orbital (φ_n), which is the k^{th} solution. Then, according to the HVM upper bound rule, the calculated energy of this wavefunction is an upper bound to the energy of the k^{th} state. Define all single excitations from this state by

$$\Phi_j^{(\ell)} = \varphi_1^{(1)}\varphi_2^{(1)} \cdots \varphi_j^{(\ell)}\varphi_{j+1}^{(1)} \cdots \varphi_n^{(k)} \qquad j \neq n \ ; \tag{24}$$

$\varphi_j^{(1)}$ was replaced by $\varphi_j^{(\ell)}$. In the case of j = n, we have $\Phi_n^{(\ell)} = \varphi_1^{(1)} \cdots \varphi_{n-1}^{(1)}\varphi_n^{(\ell)}$. The original excited state wavefunction is $\Phi_n^{(k)}$. We note that $\{\Phi_j^{(\ell)}\}_{j=1,n}^{\ell=1,m}$ gives n times m linearly independent vectors, and hence a complete basis for the supermatrix. We now propose to estimate the supermatrix in this basis. Let $\Theta_j^{(\ell)}$ be the supervector corresponding to $\Phi_j^{(\ell)}$. To evaluate B we need to calculate the second derivatives of the energy with respect to the possible changes. So let $\bar{\Theta} = \Theta_j^{(\ell)} + C'\Theta_j^{(\ell')} + C''\Theta_j^{(\ell'')}$. Then we must calculate $E(\bar{\Theta})$

$$\bar{\varphi}_i = (1 + C' + C'')\varphi_i \qquad i \neq j \tag{25a}$$

$$\bar{\varphi}_j = [\varphi_j^{(\ell)} + C'\varphi_j^{(\ell')} + C''\varphi_j^{(\ell'')}] \tag{25b}$$

$$\langle\bar{\Phi}|HP|\bar{\Phi}\rangle = (1 + C' + C'')^{n-1}[H_{\ell\ell}^j + C'^2 H_{\ell'\ell'}^j + C''^2 H_{\ell''\ell''}^j] \tag{25c}$$

and

$$\langle\bar{\Phi}|P|\bar{\Phi}\rangle = (1 + C' + C'')^{n-1}[M_{\ell\ell}^j + C'^2 M_{\ell'\ell'}^j + C''^2 M_{\ell''\ell''}^j] \ . \tag{25d}$$

The cross terms vanish since these are HVM solutions (another virtue thereof). Now

$$E(C', C'') = \frac{H_{\ell\ell}^j + C'^2 H_{\ell'\ell'}^j + C''^2 H_{\ell''\ell''}^j}{M_{\ell\ell}^j + C'^2 M_{\ell'\ell'}^j + C''^2 M_{\ell''\ell''}^j} \tag{26}$$

Further

$$E(0, 0) = E[\Theta_j^{(\ell)}] = H_{\ell\ell}^j / M_{\ell\ell}^j = \epsilon_j^{(\ell)}. \tag{27}$$

Some manipulation gives

$$\left.\frac{\partial E}{\partial C'}\right|_{\substack{C'=0\\C''=0}} = \left.\frac{\partial^2 E}{\partial C'\,\partial C''}\right|_{\substack{C'=0\\C''=0}} = 0 \tag{28}$$

and

$$\left.\frac{\partial^2 E}{\partial C'^2}\right|_{\substack{C'\\C''}} = \frac{2M^j_{\ell'\ell'}}{M^j_{\ell\ell}}\left[\frac{H^j_{\ell'\ell'}}{M^j_{\ell'\ell'}} - \frac{H^j_{\ell\ell}}{M^j_{\ell\ell}}\right]$$

$$= \frac{2M^j_{\ell'\ell'}}{M^j_{\ell\ell}}\{E[\theta_j^{(\ell')}] - E[\theta_j^{(\ell)}]\} \tag{29}$$

$$= \frac{2M^j_{\ell'\ell'}}{M^j_{\ell\ell}}[\epsilon_j^{(\ell')} - \epsilon_j^{(\ell)}] \ .$$

The conclusion from all this is that if the supermatrix at convergence is expressed in the basis of HVM single excitations, then it has the form

$$\hat{B} = \left[\begin{array}{cccc|ccc|ccc|ccc}
\Delta_1^m & & & & & & & & & & & & \\
 & \Delta_1^{m-1} & & 0 & & & & & & & & & \\
 & & \ddots & & & & & & & & & & \\
 0 & & & \Delta_1^2 & & & & & & & & & \\
 & & & \Delta_1^1 & & & & & & & & & \\
\hline
 & & & & \Delta_2^m & & & & & & & & \\
 & & & & & \ddots & 0 & & & & & & \\
 & & & & 0 & & \Delta_2^1 & & & & & & \\
\hline
 & & & & & & & \Delta & & 0 & & & \\
 & & & & & & & 0 & \ddots & & & & \\
 & & & & & & & & 0 & \Delta & & & \\
\hline
 & & & & & & & & & & \Delta_n^m & & \\
 & & & & & & & & & & & \ddots & 0 \\
 & & & & & & & & & & 0 & & \Delta_n^1
\end{array}\right]$$

where $\Delta_j^{\ell'} = M_{\ell\ell}^j[\epsilon_j^{(\ell')} - \epsilon_j^{(1)}]$ $\qquad j \neq n$

$$\Delta_n^{\ell'} = M_{\ell\ell}^n[\epsilon_n^{(\ell')} - \epsilon_n^{(k)}]$$

and we have taken $\ell = 1$ in Eq. (29) and taken out the factor $2/M_{11}^j =$ $2/\text{DENOM}$ from each term.

To examine the signs and magnitudes of these diagonal values, we rely on the following observations.

a) $\Delta_j^1 = 0 \qquad j \neq n$

b) $\Delta_n^k = 0$

c) $M_{\ell\ell}^j$ will be zero for as many values of ℓ as the number of orbitals with which φ_j is antisymmetrically coupled.

d) Since all the orbitals except $\varphi_n^{(k)}$ are the lowest solution to their HVM equation, then

$$\Delta_j^\ell = M_{\ell\ell}^j [\epsilon_j^{(\ell)} - \epsilon_j^{(1)}] \geq 0 \quad \text{for} \quad j \neq n$$

and especially

$$\Delta_n^\ell = M_{\ell\ell}^n [\epsilon_n^{(\ell)} - \epsilon_n^{(k)}] \geq 0 \qquad \ell \geq k$$

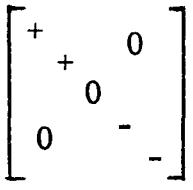
$$\Delta_n^\ell = M_{\ell\ell}^n [\epsilon_n^{(\ell)} - \epsilon_n^{(k)}] < 0 \qquad \ell > k$$

For this we can conclude

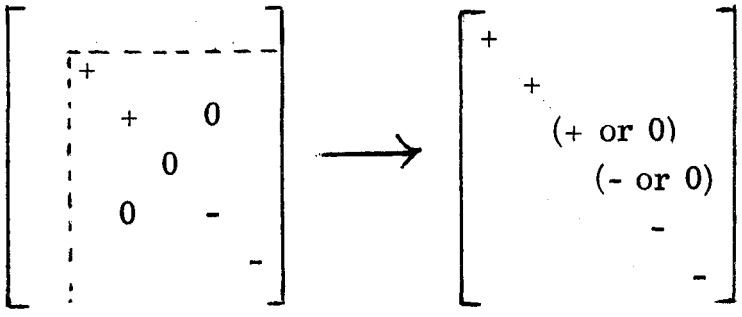
a) The number of zero diagonal values is exactly the number of zero eigenvalues predicted from renormalization and antisymmetry.

b) The number of negative diagonal values is exactly the number of lower states predicted by the HVM upper bound rule.

c) Further, suppose we are solving for a single excitation state. Then all of the negative diagonal values will be in the same orbital block, i.e., the n^{th} one, like



Then we consider expanding this block to include the whole B matrix, one row and column at a time, so:



MacDonald's theorem[13] says that the new eigenvalues are partitioned by the old eigenvalues, and in specific the p^{th} lowest eigenvalue for m rows and columns is always greater than (or equal to) the p^{th} lowest eigenvalue for any larger number of rows and columns. This means that for single excitation states the number of negative eigenvalues of the entire B matrix is always at least as large as the number of lower states as predicted by the HVM upper bound rule.

We have seen that <u>if</u> the HVM method and the supermatrix method agree on the number of lower states one can confidently bet his oatmeal cookies that he has the optimum excited state wavefunction. But what if they don't agree?

a) The supermatrix method will always predict the larger number of the lower states.

b) It may still be a decent excited state wavefunction if there is a lower, double excitation state [as in Be atom $(2p)^2$ vs 2s2p]. No one has proved that the states are now rigorously placed in an upper bound ladder. It would be very interesting to know of what help the supermatrix can be here.

c) If there is more than one extra negative eigenvalue, one is probably in trouble. One might try changing the spin coupling, making (or unmaking) symmetry functions, or basically starting over.

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APPENDIX IV.

Unique Orbitals for Two Electrons and a General One-Dimensional Representation

As explained in the preceding chapter, the spatial part of the wavefunction is written

$$\Psi^{\lambda}_{\text{space}} = \tfrac{1}{2} \sum_{\mu,\nu} (\lambda \,|\, \mu\nu)^2 O^{\mu} O^{\nu} [1 + (12)] \varphi_1(1) \varphi_2(2)$$
$$= \sum_{\mu} [\psi^1_{\mu} \psi^2_{\gamma_\mu} \pm \psi^2_{\gamma_\mu} \psi^1_{\mu}] \,, \tag{1}$$

where $\psi^i_{\mu} = O^{\mu} \varphi_i$, and γ_{μ} is the uniquely defined representation (one for each μ) that satisfies $(\lambda \,|\, \mu\gamma_{\mu})^2 = 1$ for fixed given λ. The purpose of this appendix will be to describe the "nonuniqueness" transformations that change the orbitals but not the energy and to illustrate how one solves for the optimum ("unique") orbitals through these transformations.

A. The Denominator:

1. Singlet Symmetric: The wavefunction is

$$\Psi = \sum_{\mu} [\psi^1_{\mu} \psi^2_{\mu} + \psi^2_{\mu} \psi^1_{\mu}] \,. \tag{2}$$

The only nonuniqueness transformation is of the (x, 1/x) type.

$$\bar{\varphi}_1 = 1/N_1 \sum_{\mu} x_{\mu} \psi^1_{\mu} \,, \qquad \bar{\varphi}_{\nu} = 1/N_2 \sum_{\mu} (1/x_{\mu}) \psi^2_{\mu} \,. \tag{3}$$

The terms N_1 and N_2 are just normalization factors to keep the new orbitals normalized:

$$N_1^2 = \langle \sum_\mu x_\mu \psi_\mu^1 | \sum_\nu x_\nu \psi_\nu^1 \rangle = \sum_\mu x_\mu^2 S_\mu^{22} \tag{4a}$$

$$N_2^2 = \sum_\mu (1/x_\mu^2) S_\mu^{22}, \tag{4b}$$

where $S_\mu^{ij} = \langle \psi_\mu^i | \psi_\mu^i \rangle$. Now we are ready to evaluate the denominator, which is the quantity to be maximized to evaluate the x_μ's.

$$\langle \bar{\varphi}_1 \bar{\varphi}_2 | P | \bar{\varphi}_1 \bar{\varphi}_2 \rangle = \overline{\text{DENOM}} = \frac{\langle \varphi_1 \varphi_2 | P | \varphi_1 \varphi_2 \rangle}{N_1^2 N_2^2} = \frac{\text{DENOM}}{N_1^2 N_2^2} . \tag{5}$$

The criterion maximizing $\overline{\text{DENOM}}$ is $\partial \overline{\text{DENOM}}/\partial x_\mu = 0$. This is the same as minimizing the product $R \equiv N_1^2 N_2^2$ since the term DENOM is fixed. So the equations

$$\frac{\partial R}{\partial x_\mu} = \frac{\partial [N_1^2 N_2^2]}{\partial x_\mu} = 0 \tag{6}$$

provide g (the order of the group and the number of representations) equations in g unknowns, but with zero data. Hence there is an extra (unspecified) degree of freedom in the solution of these equations. We could set $x_1 = 1$ and solve for the rest, or we could minimize R with some constraint. A convenient constraint is $N_2^2 = 1$. The variational condition (6) then becomes

$$\frac{\partial}{\partial x_\mu} [R - f(N_2^2 - 1)] = \frac{\partial N_1^2}{\partial x_\mu} - f \frac{\partial N_2^2}{\partial x_\mu} = 0 . \tag{6'}$$

Comparing with Eq. (4), this yields

$$2x_\alpha S_\alpha^{11} - f(-2/x_\alpha^3) S_\alpha^{22} = 0 \tag{7a}$$

$$x_\alpha^4 = -f S_\alpha^{22} / S_\alpha^{11} . \tag{7b}$$

To eliminate f we notice that it is just a scale factor, multiplying the entire orbital φ_1 by -f and φ_2 by -1/f. Specifically, using (7b) and (4)

$$N_1^2 = (-f)^{\frac{1}{2}} \sum_\mu (S_\mu^{11} S_\mu^{22})^{\frac{1}{2}} \tag{8a}$$

$$N_2^2 = (-f)^{-\frac{1}{2}} \sum_\mu (S_\mu^{11} S_\mu^{22})^{\frac{1}{2}} . \tag{8b}$$

Hence R is independent of f, so we arbitrarily set f = -1 and forget it. The final result is now

$$x_\alpha = (S_\alpha^{22}/S_\alpha^{11})^{\frac{1}{4}} . \tag{9}$$

2. Triplet Symmetric: For this case there are two types of transformations, (x, 1/x) and orbital shape. The wavefunction is

$$\Psi = \sum_\mu [\psi_\mu^1 \psi_\mu^2 - \psi_\mu^2 \psi_\mu^1] . \tag{10}$$

The (x, 1/x) transformation gives

$$\bar{\varphi}_1 = 1/N_1 \sum_\mu x_\mu \psi_\mu^1 , \qquad \bar{\varphi}_2 = 1/N_2 \sum_\mu (1/x_\mu)\psi_\mu^2 . \tag{11}$$

Finally, $\bar{\varphi}_2$ can be added to φ_1 in pieces (or vice versa)

$$\bar{\bar{\varphi}}_1 = 1/N_1 \sum_\mu [x_\mu \psi_\mu^1 + z_\mu \psi_\mu^2] . \tag{11'}$$

The values of the x_μ's and z_μ's are to be found through Eq. (6') as before. Now

$$N_1^2 = \sum_\mu [x_\mu^2 S_\mu^{11} + z_\mu^2 S_\mu^{22} + 2x_\mu z_\mu S_\mu^{12}] \tag{12a}$$

$$N_2^2 = \sum_\mu (1/x_\mu^2) S_\mu^{22} . \tag{12b}$$

The variation of z_α gives

$$\partial/\partial z_\alpha [N_1^2 - fN_2^2] = 2z_\alpha S_\alpha^{22} + 2x_\alpha S_\alpha^{12} = 0 \tag{13}$$

or

$$z_\alpha = -x_\alpha S_\alpha^{12}/S_\alpha^{22} . \tag{14}$$

Substituting into Eq. (12a) gives

$$N_1^2 = \sum_\mu{}' x_\mu^2 [S_\mu^{11} - (S_\mu^{12})^2/S_\mu^{22}] . \tag{15}$$

Finally, Eq. (6′) with f = -1 gives

$$x_\alpha = \left[\frac{(S_\alpha^{22})^2}{S_\alpha^{11} S_\alpha^{22} - (S_\alpha^{12})^2} \right]^{\frac{1}{4}} . \tag{16}$$

3. Singlet and Triplet Nonsymmetric: The situation now becomes slightly more complicated. The wavefunction is given by Eq. (1) with $x_\mu \neq \mu$. The (x, 1/x) transformation appears as

$$\bar{\varphi}_1 = 1/N_1 \sum_\mu x_\mu \psi_\mu^1, \qquad \bar{\varphi}_2 = 1/N_2 \sum_\mu (1/x_\mu)\psi_{\gamma_\mu}^2 . \tag{17}$$

To accomplish the shape-orbital transformations, we rearrange the representations such that $\mu \leq g/2$ implies that $\gamma_\mu > g/2$. Then define $\omega = 1$ if the state is a triplet and -1 if it is a singlet. The shape-orbital transformation is now given by

$$\bar{\bar{\varphi}}_1 = 1/N_1 \{ \sum_\mu x_\mu \psi_\mu^1 + \sum_{\mu=1}^{g/2} z_\mu [(1/x_{\gamma_\mu})\psi_\mu^2 + (\omega/x_\mu)\psi_{\gamma_\mu}^2] \} . \tag{18}$$

Now

$$N_1^2 = \sum_{\mu} x_\mu^2 S_\mu^{11} + \sum_{\mu=1}^{g/2} \{z_\mu [(S_\mu^{22}/x_{\gamma_\mu}^2) + (S_{\gamma_\mu}^{22})] + 2z_\mu [(x_\mu/x_{\gamma_\mu}) S_\mu^{12} + (x_{\gamma_\mu}/x_\mu)\omega S_{\gamma_\mu}^{12}]\}, \tag{19}$$

N_2^2 is given by Eq. (4b) as before.

The z_α differentiation as in Eq. (13) gives

$$z_\alpha = - \frac{(x_\alpha^2 S_\alpha^{12} + \omega x_{\gamma_\alpha}^2 S_{\gamma_\alpha}^{12}) x_\alpha x_{\gamma_\alpha}}{(x_\alpha^2 S_\alpha^{22} + x_{\gamma_\alpha}^2 S_{\gamma_\alpha}^{22})} \tag{20}$$

So now

$$N_1^2 = \sum_{\mu} x_\mu^2 S_\mu^{11} - \sum_{\mu=1}^{g/2} \frac{[x_\mu^2 S_\mu^{12} + \omega x_{\gamma_\mu}^2 S_{\gamma_\mu}^{12}]^2}{[x_\mu^2 S_\mu^{22} + x_{\gamma_\mu}^2 S_{\gamma_\mu}^{22}]} . \tag{21}$$

Finally, if we set

$$A_\alpha = [x_\alpha^2 S_\alpha^{12} + \omega x_{\gamma_\alpha}^2 S_{\gamma_\alpha}^{12}] \qquad \alpha \leq g/2$$

$$B_\alpha = [x_\alpha^2 S_\alpha^{22} + x_{\gamma_\alpha}^2 S_{\gamma_\alpha}^{22}] , \tag{22}$$

Then

$$\frac{\partial}{\partial x_\alpha} [N_1^2 - f(N_2^2 - 1)] = 2x_\alpha S_\alpha^{11} - 4x_\alpha S_\alpha^{12} A_\alpha/B_\alpha + 2x_\alpha S_\alpha^{22} A_\alpha^2/B_\alpha^2 + (2f/x_\alpha^3) S_{\gamma_\alpha}^{22} = 0 , \tag{23a}$$

and

$$\frac{\partial}{\partial x_{\gamma_\alpha}} [N_1^2 - f(N_2^2 - 1)] = 2x_{\gamma_\alpha} S_{\gamma_\alpha}^{11} - 4\omega x_{\gamma_\alpha} S_{\gamma_\alpha}^{12} A_\alpha/B_\alpha + 2x_{\gamma_\alpha} S_{\gamma_\alpha}^{22} A_\alpha^2/B_\alpha^2 + (2f/x_{\gamma_\alpha}^3) S_\alpha^{22} = 0. \tag{23b}$$

Now Eqs. (23a) and (23b) may be solved simultaneously for x_α and x_{γ_α} after setting f = -1. The two equations are coupled fourth-degree polynomials in x_α^2 and $x_{\gamma_\alpha}^2$ and appear to be best solved numerically.

B. The Orbital Energies

1. Singlet Symmetric: For this simple case there are no transformations left after maximizing the denominator. The only thing to be done is to be sure that for each symmetry (μ) the lowest energy piece (either ψ_μ^1 or ψ_μ^2) be used for φ_1 and the highest for φ_2.

2. Triplet Symmetric: After the denominator is maximized, we have $S_\mu^{12} = 0$ and $S_\mu^{11} = S_\mu^{22}$. The further unitary transformation that changes neither the denominator nor the energy is

$$\begin{aligned} \varphi_1' &= \sum_\mu [\cos\theta_\mu \psi_\mu^1 + \sin\theta_\mu \psi_\mu^2] \\ \varphi_2' &= \sum_\mu [-\sin\theta_\mu \psi_\mu^1 + \cos\theta_\mu \psi_\mu^2] \,. \end{aligned} \tag{24}$$

Evaluation of the various overlaps gives $(S_\mu^{12})' = 0$, $(S_\mu^{11})' = S_\mu^{11} = (S_\mu^{22})' = S_\mu^{22}$ so that the denominator is maximized for any values of the θ_μ's. This was just to check that the denominator is independent of the θ_μ's.

To specify the θ_μ's we construct the orbital energy of φ_2,

$$\begin{aligned} \epsilon_2 &= E_2 - E_1 = E - \langle \varphi_1' | h | \varphi_1' \rangle \\ &= E - \sum_\mu [\cos^2\theta_\mu H_\mu^{11} + \sin^2\theta_\mu H_\mu^{22} + 2\cos\theta_\mu \sin\theta_\mu H_\mu^{12}] \,, \end{aligned} \tag{25}$$

where $H_\mu^{ij} = \langle \psi_\mu^i | h | \psi_\mu^j \rangle$. Now ϵ_2 is to be the best possible approximation to the vertical ionization energy, hence it is to be maximized:

$\partial \epsilon_2 / \partial \theta_\alpha = 0$. This gives

$$\tan 2\theta_\alpha = \frac{2H_\alpha^{12}}{H_\alpha^{11} - H_\alpha^{22}} \quad . \tag{26}$$

To insure that ϵ_2 is a maximum (rather than a minimum), θ_μ is replaced by $(\theta_\mu + \pi/2)$ if $\cos 2\theta_\mu \cdot (H_\mu^{11} - H_\mu^{22}) > 0$.

3. Singlet and Triplet Nonsymmetric: Once again the situation is more complicated. After the denominator is maximized, the unitary transformation that remains is

$$\begin{aligned} \varphi_1' &= \sum_{\mu=1}^{g/2} \{\cos\theta_\mu [\psi_\mu^1 + \psi_{\gamma_\mu}^1] + \sin\theta_\mu [\psi_\mu^2 + \omega\psi_{\gamma_\mu}^2]\} \\ \varphi_2' &= \sum_{\mu=1}^{g/2} \{-\sin\theta_\mu [\psi_\mu^1 + \omega\psi_{\gamma_\mu}^1] + \cos\theta_\mu [\psi_\mu^2 + \psi_{\gamma_\mu}^2]\} \end{aligned} \tag{27}$$

One may verify that the denominator and energy are independent of the θ_μ's. To find the optimum θ_μ's the same procedure is adopted as in the previous case. First the orbital energy is defined:

$$\begin{aligned} \epsilon_2 = E - \langle \varphi_1' | h | \varphi_1' \rangle = E - \sum_{\mu=1}^{g/2} \{ &\cos^2\theta_\mu [H_\mu^{11} + H_{\gamma_\mu}^{11}] \\ &+ \sin^2\theta_\mu [H_\mu^{22} + H_{\gamma_\mu}^{22}] + 2\sin\theta_\mu \cos\theta_\mu [H_\mu^{12} + \omega H_{\gamma_\mu}^{12}]\} \end{aligned} \tag{28}$$

Then $\partial \epsilon_2 / \partial \theta_\mu = 0$ yields

$$\tan 2\theta = \frac{2[H_\mu^{12} + \omega H_{\gamma_\mu}^{12}]}{[H_\mu^{11} + H_{\gamma_\mu}^{11} - H_\mu^{22} - H_{\gamma_\mu}^{22}]} \tag{29}$$

Once again θ_μ is chosen such that $\cos 2\theta_\mu \cdot [H_\mu^{11} + H_{\gamma_\mu}^{11} - H_\mu^{22} - H_{\gamma_\mu}^{22}] < 0$.

C. Illustration: As has been emphasized repeatedly, the energy is determined by the many-electron wavefunction and therefore only indirectly by the orbitals. The role of this Appendix is to illustrate how the orbitals are found after the wavefunction is known.

Consider the case of ^1A wavefunction for the point group C_2 written in terms of natural orbitals[1]

$$\Psi = [\, n_A^2 A^2 - n_{A'}^2 A'^2 + n_B^2 B^2 - n_{B'}^2 B'^2 \,] \,. \tag{30}$$

We now decompose this into orbitals

$$\begin{aligned} \Psi = \tfrac{1}{2}[1 + (12)]\{&(n_A A + n_{A'} A')(n_A A - n_{A'} A') \\ &+ (n_B B + n_{B'} B')(n_B B - n_{B'} B')\} \end{aligned} \tag{31}$$

$$\varphi_1 = (n_A A + n_{A'} A') + (n_B B + n_{B'} B')$$

$$\varphi_2 = (n_A A - n_{A'} A'') + (n_B B - n_{B'} B') \,.$$

The decomposition chosen makes the two orbitals have the same percentage A character and the same percentage B character. We may check to see that the denominator is maximized for this choice [cf. Eq. (9)].

$$x_A = \left[\frac{(n_A^2 + n_{A'}^2)}{(n_A^2 + n_{A'}^2)} \right]^{\frac{1}{4}} = 1 \,, \tag{32}$$

and similarly for the B components. Dividing the wavefunction equally between the two orbitals (as we have just done) makes the orbitals as representative of the wavefunction as possible. A very similar analysis applies to the other possible symmetries.

References

1. The orthonormal natural orbitals are A, A′ and B, B′ of A and B symmetry, respectively. The coefficients (e.g., n_A^2) are the occupation numbers.

APPENDIX V.

Nonuniqueness for Spin-Projected Generalized Spin Orbitals

Lunell[1] discusses the use of spin-projected generalized spin orbitals to describe the ground states of H^-, He, Li^+, and Be^{++}. The essence of the technique is that each orbital is assigned an up-spin and down-spin component:

$$\begin{aligned} \varphi_1 &= \psi_+^1\alpha + \psi_-^1\beta \\ \varphi_2 &= \psi_+^2\alpha + \psi_-^2\beta \quad . \end{aligned} \tag{1}$$

Then the two-electron wavefunction is obtained by spin and permutation projection[2]

$$\Psi = \tfrac{1}{2}[(\psi_+^1\psi_-^2 + \psi_-^2\psi_+^1) + (\psi_-^1\psi_+^2 + \psi_+^2\psi_-^1)](\alpha\beta - \beta\alpha) \; . \tag{2}$$

Let us examine the nonuniqueness transformations that exist for this type of wavefunction.

The (x, 1/x) transformation is easy to describe

$$\begin{aligned} \bar{\varphi}_1 &= x\psi_+^1\alpha + \psi_-^1\beta \\ \bar{\varphi}_2 &= \psi_+^2\alpha + (1/x)\psi_-^2\beta \; . \end{aligned} \tag{3}$$

The shape transformation is simply

$$\bar{\varphi}_1 = \varphi_1 + z[\psi_+^2\alpha - \psi_-^2\beta] \; . \tag{4}$$

After (3) and (4) are resolved by maximizing the denominator, there remains the unitary shape transformation,

$$\begin{aligned} \varphi_1' &= \cos\theta\ \varphi_1 + \sin\theta[\psi_+^2\alpha - \psi_-^2\beta] \\ \varphi_2' &= -\sin\theta[\psi_+^1\alpha - \psi_-^1\beta] + \cos\theta\ \varphi_2 \; . \end{aligned} \tag{5}$$

The mixing angle θ is to be determined from the orbital energy.

Lunell noticed that there are three degrees of freedom in the orbitals: Eqs. (3), (4), (5). But he had not identified the procedure of maximizing the denominator as the way of removing most of the arbitrariness in the orbitals. He tried to do the entire task with the orbital energies. It is easy to see how he obtained his admittedly nonsensical orbitals.

The orbital energy technique, as explained in the preceding Appendix (IV), attempts to make ϵ_2 as high as possible and therefore $\langle \varphi_1 | h | \varphi_1 \rangle$ as low as possible. Suppose $\langle \psi_+^1 | h | \psi_+^1 \rangle$ gave the lowest value of the choices $(\psi_+^1, \psi_+^2, \psi_-^1, \psi_-^2)$ and the same-spin linear combinations. The orbital energy procedure would then set $x = \infty$ in Eq. (3), and after renormalization

$$\varphi_1 = \psi_+^1 \alpha, \qquad \varphi_2 = \psi_+^2 \alpha, \qquad \Psi = 0. \tag{6}$$

The procedure of maximizing the denominator will avoid this meaningless result, and allow a comprehensible description of the orbitals.

References

1. S. Lunell, Phys. Rev. A 1, 360 (1970).

2. Lunell uses the form

$$\Psi = \tfrac{1}{2}[(\psi_+^1\psi_-^2 + \psi_-^2\psi_+^1) - (\psi_-^1\psi_+^2 + \psi_+^2\psi_-^1)](\alpha\beta - \beta\alpha).$$

The sign between the two sets of spatial terms is irrelevant. The plus sign is chosen here [Eq. (2)] to make the projection operator resemble more the work in the previous Appendix:

$$P_{space} = O^+(1)O^-(2) + O^-(1)O^+(2) .$$

The change in sign from Eq. (2) can be accomplished by a change in sign of either ψ_-^1 or ψ_+^2.

APPENDIX VI

Coefficients of the PGVB orbitals for the various Σ states of H_2 in terms of the 16 basis function set as described in Table I of Part 1.

H2 1 1-SIGMA-G+ PGI 16BF (X=1S STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.572920	0.476453	0.462988	0.408015	0.364377	0.333426	0.313140
0.116192	0.350162	0.383603	0.516618	0.579192	0.590401	0.561898
0.095323	-0.152151	-0.138052	-0.051351	0.009135	0.070354	0.164347
-0.129333	-0.361004	-0.311640	-0.041833	0.068513	0.078078	0.025407
-0.001073	-0.160216	-0.158993	-0.086258	-0.043492	-0.053064	0.010505
0.009195	0.072200	0.076066	0.079706	0.073670	0.064962	0.053448
-0.056237	-0.101745	-0.091538	-0.011612	0.042302	0.063605	0.070408
0.044727	-0.013296	-0.018595	-0.031469	-0.040018	-0.051303	-0.046922
0.275815	0.211804	0.199039	0.135176	0.086278	0.050963	0.027608
-0.022351	0.018741	0.026147	0.065424	0.101461	0.107882	0.088674
0.090867	0.204596	0.170515	-0.000818	-0.089748	-0.104735	-0.089987
0.038513	0.368313	0.334495	0.135120	0.062452	0.043653	0.045728
0.024921	0.158370	0.153313	0.064892	0.016628	0.033441	-0.012767
-0.122211	-0.082164	-0.080352	-0.074750	-0.069807	-0.062959	-0.052476
0.037132	-0.081692	-0.081917	-0.056511	-0.045762	-0.051022	-0.058327
-0.048599	-0.032069	-0.027936	0.004830	0.029009	0.034672	0.044146

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.303070	0.301694	0.306040	0.308460	0.308713	0.308616	0.308423
0.521039	0.484515	0.488041	0.492099	0.493143	0.492984	0.492093
0.255067	0.327943	0.313088	0.296914	0.293578	0.294270	0.296915
-0.021832	-0.024480	0.009229	0.031153	0.033681	0.030956	0.025965
0.021424	-0.026400	-0.058098	-0.033138	-0.016530	-0.007906	-0.001181
0.039783	0.018068	0.013272	0.008974	0.006302	0.004794	0.003181
0.074118	0.092970	0.093381	0.070749	0.052295	0.039572	0.025063
-0.046709	-0.058881	-0.065086	-0.042135	-0.024994	-0.015441	-0.007328
0.013041	0.001285	-0.001621	-0.000827	-0.000279	-0.000173	-0.000165
0.052551	-0.005354	-0.017901	-0.004228	-0.000632	-0.000258	-0.000506
-0.052437	0.009965	0.025430	0.003839	-0.000174	-0.000051	0.001266
0.029085	-0.019632	-0.027438	-0.002653	-0.000101	-0.001336	-0.002583
-0.005003	0.052863	0.072256	0.030600	0.013514	0.007143	0.002831
-0.039634	-0.020713	-0.008320	-0.001098	-0.000049	0.000017	-0.000084
-0.061039	-0.033828	-0.014858	-0.005459	-0.002232	-0.000446	0.000684
0.042578	0.015451	-0.007524	-0.010116	-0.007280	-0.004986	-0.002090

H2 1 1-SIGMA-G+ PGI 16BF (X=1S STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
-0.016915	-0.026411	-0.026661	-0.025072	-0.014473	-0.001965	0.005347
0.239793	0.104198	0.080874	-0.020849	-0.075492	-0.090357	-0.080387
0.105508	0.363C76	0.352962	0.289287	0.254665	0.214703	0.168247
0.080910	0.355711	0.312090	0.065245	-0.032923	-0.034258	-0.033963
0.028804	0.147504	0.147061	0.086308	0.042823	0.C10267	0.057214
0.030920	-0.035644	-0.040452	-0.051268	-0.053364	-0.052106	-0.045938
0.023147	0.116472	0.11C000	0.042432	-0.009439	-0.035733	-0.052134
-0.006279	0.006777	0.009020	0.013610	0.020721	0.028651	0.046399
0.280187	0.238225	0.237270	0.247767	0.263626	0.279673	0.295776
0.378312	0.435537	0.438239	0.430344	0.402239	0.389365	0.411460
0.109515	0.006687	0.044753	0.238754	0.353548	0.397717	0.370885
-0.086984	-0.373825	-0.334335	-0.111708	-0.026862	-0.013406	0.029076
-0.025911	-0.136988	-0.134743	-0.064842	-0.017297	0.010151	-0.051694
0.082094	0.045608	0.044737	0.046312	0.049501	0.050059	0.045428
-0.003979	0.066995	0.063491	0.025691	0.012899	0.023470	0.038487
0.011386	0.035844	0.034878	0.013029	-0.009712	-0.025938	-0.024628

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.008153	0.006597	0.004651	0.001237	0.000358	0.000212	0.000182
-0.050380	0.003790	0.016146	0.004670	0.000552	0.000382	0.000558
0.106848	0.013480	-0.015776	-0.003794	0.000354	-0.000268	-0.001397
-0.016881	0.027100	0.030374	0.004367	0.000439	0.001889	0.002856
0.042913	-0.039258	-0.069063	-0.031924	-0.014418	-0.007861	-0.003140
-0.035995	-0.020183	-0.008645	-0.001123	-0.000081	0.000005	-0.000091
-0.059984	-0.035720	-0.016747	-0.006048	-0.002209	-0.000409	0.000741
0.049849	0.020786	-0.005244	-0.010161	-0.007744	-0.005343	-0.002295
0.306421	0.310749	0.308097	0.307045	0.307355	0.307727	0.308152
0.450297	0.490636	0.490499	0.489015	0.488917	0.489525	0.490809
0.315960	0.264010	0.281671	0.299114	0.303041	0.302603	0.300075
0.069479	0.071079	0.038171	0.015616	0.012922	0.015676	0.020889
-0.055658	0.014973	0.056535	0.035758	0.019136	0.010227	0.003129
0.035865	0.017239	0.013125	0.008967	0.006294	0.004785	0.003176
0.053199	0.086259	0.091368	0.070686	0.052385	0.039673	0.025122
-0.029015	-0.052003	-0.063317	-0.042663	-0.025567	-0.015837	-0.007465

H2 2 1-SIGMA-G+ PGI 16BF (E=2S ; F=2P STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.467154	0.381070	0.369689	0.326210	0.298470	0.267931	0.360487
0.230110	0.375363	0.394364	0.464135	0.491079	0.473115	0.580075
0.159052	-0.008139	-0.005675	0.037968	0.102320	0.200732	0.163576
0.012720	-0.080019	-0.065880	0.007919	0.007143	-0.208328	0.176716
-0.073948	-0.077831	-0.075491	-0.052018	-0.043054	-0.013776	-0.133781
0.019592	0.044744	0.045750	0.043146	0.035830	0.022525	0.035325
-0.005586	-0.008743	-0.003152	0.034655	0.055130	-0.025258	0.119885
0.003940	-0.026433	-0.029825	-0.042224	-0.051283	-0.050064	-0.052692
0.283844	0.218528	0.208429	0.164039	0.132028	0.117385	-0.022736
0.083062	0.164183	0.173219	0.203207	0.210104	0.197539	-0.008053
-0.116863	-0.005158	-0.010525	-0.045892	-0.059966	-0.079522	-0.000838
-0.031337	0.116171	0.108702	0.058440	0.060283	0.253851	-0.160457
0.078062	0.067826	0.063970	0.036592	0.030486	0.010254	0.144674
-0.062732	-0.046277	-0.045117	-0.039797	-0.035164	-0.033471	0.005689
0.015019	-0.047656	-0.050561	-0.053241	-0.059839	-0.147885	0.049774
-0.016554	0.004026	0.007034	0.022834	0.029507	0.032155	-0.007220

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.364254	0.350612	0.338441	0.320212	0.305818	0.303490	0.308094
0.570806	0.547920	0.529283	0.503930	0.489317	0.484044	0.491106
0.165052	0.175684	0.194767	0.235318	0.274687	0.297342	0.298527
0.159953	0.133811	0.108731	0.066214	0.031994	0.017896	0.023331
-0.200419	-0.260632	-0.209137	-0.101639	-0.044315	-0.003496	0.000997
0.025901	0.018521	0.014885	0.011956	0.007097	0.001259	-0.000066
0.095799	0.082051	0.067526	0.040199	0.015681	-0.001244	-0.001084
-0.063982	-0.058620	-0.057937	-0.070185	-0.038704	-0.005947	-0.000287
-0.029949	-0.003271	0.017624	0.046419	0.066403	0.055211	0.012334
-0.038145	-0.008592	0.025472	0.074915	0.101165	0.085142	0.019543
0.013401	0.040662	0.054253	0.061183	0.061644	0.046666	0.010389
-0.138867	-0.094583	-0.066799	-0.033075	-0.009909	0.001915	0.001191
0.216364	0.273661	0.222061	0.115369	0.057424	0.012207	0.000166
0.017910	0.023760	0.023105	0.018841	0.011520	0.003711	0.002075
0.078607	0.102962	0.107069	0.089943	0.058451	0.025084	0.001982
-0.060347	-0.118871	-0.125383	-0.096015	-0.056318	-0.013641	-0.000310

H2 2 1-SIGMA-G+ PGI 16BF (E=2S ; F=2P STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.055228	0.041193	0.039943	0.038847	0.040631	0.072651	0.019723
-0.172559	-0.030363	-0.011936	0.058420	0.088441	0.115632	-0.009308
-0.425345	-0.511826	-0.486973	-0.336044	-0.205558	-0.092525	0.154096
0.199555	-0.158612	-0.158253	-0.092782	-0.082914	0.118508	-0.078357
0.476054	0.414699	0.410869	0.459953	0.510486	0.448074	0.373552
-0.030066	0.002592	0.004962	0.009326	0.008856	0.011580	-0.016108
-0.015740	-0.090728	-0.087760	-0.038869	0.002768	0.103454	0.017657
0.026167	0.006737	0.003788	0.002364	0.015750	0.037317	0.080308
-0.124813	-0.108915	-0.108670	-0.115141	-0.126405	-0.167259	-0.101947
0.012090	-0.134446	-0.152854	-0.225366	-0.269876	-0.337090	-0.266917
0.133228	0.178447	0.149541	-0.013101	-0.142765	-0.250796	-0.414343
0.340909	0.530739	0.503586	0.321045	0.232822	0.040838	0.455264
0.227670	0.446132	0.472328	0.515272	0.515812	0.533048	0.195102
-0.027889	-0.000541	0.001162	0.003599	0.001993	0.004318	-0.024494
0.040361	0.006578	0.011740	0.055996	0.063208	0.034970	-0.424220
-0.001365	0.000581	0.001657	0.018356	0.032902	-0.001764	-0.044837

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.036547	0.056169	0.064364	0.066886	0.056879	0.030578	0.004915
-0.017536	-0.004882	0.013246	0.041229	0.048399	0.036092	0.008285
0.272244	0.316515	0.278006	0.181944	0.123839	0.073614	0.018066
0.077384	0.187284	0.245080	0.261017	0.156882	0.025703	-0.015057
0.370198	0.429527	0.354023	0.193771	0.064539	-0.035066	-0.019410
-0.016070	-0.015638	-0.015485	-0.014269	-0.008011	-0.001530	-0.000019
0.045095	0.003411	-0.019929	-0.054017	-0.097901	-0.087129	-0.004956
0.080280	0.130400	0.137138	0.090976	0.008125	-0.039370	-0.000825
-0.092143	-0.072601	-0.058469	-0.052025	-0.062507	-0.066711	-0.066219
-0.238753	-0.182108	-0.145256	-0.116947	-0.134708	-0.163849	-0.224593
-0.328236	-0.220264	-0.197401	-0.219971	-0.231926	-0.228990	-0.301497
0.376384	0.275050	0.258280	0.274153	0.276043	0.310853	0.440848
-0.098709	-0.263055	-0.191690	0.057230	0.337872	0.545802	0.781907
-0.028860	-0.026911	-0.022217	-0.015577	-0.008527	-0.002437	-0.000287
-0.489310	-0.460054	-0.447713	-0.459028	-0.513167	-0.511583	-0.112001
0.050998	0.132350	0.107629	-0.041409	-0.227904	-0.311691	-0.068262

H2 3 1-SIGMA-G+ PGI 16BF (H=3D ; E=2S STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	0.330608	0.304004	0.307605	0.349298	0.327859
0.0	0.0	0.403934	0.472331	0.527729	0.584811	0.541499
0.0	0.0	0.031245	0.059232	0.087639	0.140885	0.201747
0.0	0.0	-0.025559	-0.000563	0.025903	0.057748	0.071980
0.0	0.0	-0.039899	-0.051953	-0.080373	-0.082762	-0.059944
0.0	0.0	0.042935	0.040707	0.037835	0.029626	0.020326
0.0	0.0	0.018496	0.044382	0.053802	0.059146	0.065764
0.0	0.0	-0.024987	-0.042922	-0.057364	-0.034950	-0.038442
0.0	0.0	0.257143	0.192820	0.119235	0.002557	0.012124
0.0	0.0	0.167724	0.201795	0.168340	0.015067	0.029385
0.0	0.0	-0.056464	-0.080040	-0.058763	-0.028728	0.010131
0.0	0.0	0.070803	0.069933	0.061693	-0.054417	-0.054519
0.0	0.0	0.028664	0.036780	0.068485	0.076571	0.055311
0.0	0.0	-0.051528	-0.046013	-0.034500	-0.010951	-0.007844
0.0	0.0	-0.032410	-0.046717	-0.057861	-0.011940	-0.009712
0.0	0.0	0.013198	0.022523	0.017841	-0.006984	0.002932

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.307852	0.305744	0.307759	0.308614	0.308536	0.308488	0.308516
0.501361	0.486143	0.489059	0.491852	0.491961	0.491744	0.491793
0.252738	0.294291	0.298004	0.296306	0.297219	0.298639	0.299673
0.032358	0.022277	0.029060	0.030099	0.026798	0.024144	0.022359
-0.043861	-0.036066	-0.027489	-0.010051	-0.003429	-0.001288	-0.001247
0.014145	0.006290	0.003185	0.001286	0.000727	0.000438	0.000021
0.069020	0.052090	0.037001	0.018018	0.009072	0.004337	-0.000259
-0.040784	-0.030954	-0.020665	-0.006852	-0.002018	-0.000625	-0.000151
0.032947	0.022606	0.010532	0.001627	-0.000821	-0.001404	0.005659
0.052920	0.026369	0.009744	0.002099	-0.001379	-0.002241	0.008997
0.038691	0.042532	0.023999	0.004111	0.001571	0.001223	0.006037
-0.031729	-0.017622	-0.007452	-0.000121	-0.001608	-0.002281	0.000150
0.047832	0.037609	0.023679	0.005736	0.001856	0.000505	-0.001013
-0.008001	-0.002686	-0.000321	0.000337	0.000363	0.000433	0.000484
-0.022554	-0.015384	-0.005835	0.001041	0.002379	0.003253	0.002464
0.007368	-0.000845	-0.005173	-0.003959	-0.002306	-0.001600	-0.000567

H2 3 1-SIGMA-G+ PGI 16BF (H=3D ; E=2S STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	0.115016	0.126347	0.085987	0.009090	-0.036094
0.0	0.0	0.311106	0.305806	0.203808	0.069815	-0.009007
0.0	0.0	0.390922	0.327884	0.065941	-0.144719	-0.205629
0.0	0.0	1.975130	2.186297	1.643810	0.582625	-0.023119
0.0	0.0	-0.136151	0.160906	0.322395	0.365168	0.510306
0.0	0.0	0.008554	0.001210	0.003022	0.011408	0.006182
0.0	0.0	0.119405	0.318805	0.233760	-0.064066	-0.034021
0.0	0.0	-3.569876	-2.521658	-1.773620	-0.830373	-0.185020
0.0	0.0	-0.012459	-0.024313	0.009647	0.037307	-0.014902
0.0	0.0	-0.024306	-0.010535	0.080421	0.134945	-0.028524
0.0	0.0	-0.643831	-0.573227	-0.224699	0.224592	0.100212
0.0	0.0	-0.692829	-0.888818	-0.537199	-0.368885	-0.122308
0.0	0.0	-0.205425	-0.553097	-0.648856	-0.140391	0.405495
0.0	0.0	-0.010600	-0.014352	-0.008916	0.005801	0.006359
0.0	0.0	0.644386	0.783999	0.746376	0.750894	0.548892
0.0	0.0	3.689015	2.777716	2.101213	1.048578	0.335924

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
-0.030580	-0.017867	-0.009810	-0.003874	0.002916	-0.002978	-0.001150
-0.007736	-0.006716	-0.004913	-0.002142	-0.001757	-0.001717	0.001020
-0.121779	-0.026954	-0.005768	-0.003969	-0.004767	-0.004927	-0.004802
-0.163685	-0.165260	-0.094850	-0.027385	-0.013609	-0.011494	-0.004252
0.454311	0.234132	0.090917	0.005991	-0.003095	-0.005404	-0.011562
0.005211	0.002094	0.000835	0.000147	0.000057	0.000020	-0.000012
0.015561	0.020421	0.012119	0.002391	-0.002000	-0.002161	0.012718
-0.086361	-0.049544	-0.028349	-0.006668	-0.001690	-0.001724	0.006629
-0.046254	-0.063364	-0.067331	-0.067840	-0.065516	-0.058479	-0.014307
-0.121716	-0.167857	-0.176678	-0.177261	-0.171082	-0.152673	-0.037451
-0.053029	-0.174030	-0.216753	-0.233311	-0.227304	-0.203644	-0.049205
0.091109	0.249843	0.312140	0.340358	0.332613	0.298408	0.072077
0.528661	0.627702	0.644950	0.627101	0.598373	0.532323	0.130927
0.002599	0.000824	0.000567	0.000659	0.001067	0.001297	0.001779
0.430884	0.393059	0.392659	0.409257	0.437467	0.494998	0.665110
0.259882	0.258774	0.265539	0.269171	0.280137	0.312373	0.411851

H2 1 1-SIGMA-U+ PGI 16BF (B=2P STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.390883	0.337289	0.328879	0.306386	0.310709	0.320404	0.329691
0.280146	0.339498	0.346392	0.395622	0.458449	0.495619	0.505717
0.015004	-0.177606	-0.194478	-0.203222	-0.129553	-0.043972	0.038895
-0.242495	-0.514004	-0.550404	-0.585570	-0.393862	-0.211676	-0.107624
-0.048371	-0.047240	-0.054809	-0.098410	-0.026887	0.078352	0.133747
-0.002999	0.021705	0.023621	0.028123	0.030194	0.029068	0.024589
0.014838	-0.044154	-0.056354	-0.082823	-0.037212	0.018079	0.052402
0.001326	-0.031740	-0.037979	-0.069314	-0.068219	-0.043820	-0.205449
0.363868	0.265408	0.252085	0.184452	0.117426	0.066602	0.032542
0.026557	0.193245	0.213811	0.257135	0.214704	0.142423	0.069567
0.011858	0.135963	0.147654	0.154359	0.122882	0.112752	0.112403
0.229292	0.561218	0.605569	0.672289	0.492544	0.302423	0.177383
0.052033	0.036012	0.041919	0.081149	0.012725	-0.082814	-0.125414
-0.089462	-0.075239	-0.073631	-0.063726	-0.052240	-0.041484	-0.032496
-0.032166	-0.159549	-0.183364	-0.269110	-0.268605	-0.236530	-0.203928
0.009925	0.030939	0.032485	0.037559	0.060550	0.089817	0.104531

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.337726	0.344651	0.340272	0.321993	0.306833	0.305422	0.307923
0.505172	0.507668	0.511971	0.502253	0.487008	0.487447	0.490846
0.107549	0.180092	0.200583	0.225556	0.265013	0.284928	0.296616
-0.056454	-0.006554	0.022986	0.041542	0.038548	0.034578	0.025199
0.139900	0.102639	0.060558	0.014083	0.005060	0.006743	0.004028
0.019651	0.013753	0.011275	0.010047	0.005336	0.000689	-0.000105
0.065778	0.061914	0.052922	0.052484	0.040860	0.012673	0.003801
-0.007274	0.000097	-0.002593	-0.012250	-0.004788	0.006614	0.004875
0.009528	-0.020829	-0.041145	-0.070143	-0.074631	-0.047422	-0.010540
0.010831	-0.056373	-0.085300	-0.116980	-0.117535	-0.072801	-0.016585
0.100909	0.039166	-0.023954	-0.083458	-0.073836	-0.047201	-0.010660
0.107383	0.052270	0.036851	0.026041	0.014514	0.006096	-0.000269
-0.122048	-0.085428	-0.057056	-0.032756	-0.026614	-0.012601	0.000279
-0.025830	-0.018298	-0.015279	-0.014137	-0.009716	-0.003830	-0.000629
-0.177040	-0.139803	-0.116412	-0.093284	-0.063693	-0.025707	-0.003203
0.103146	0.084843	0.067320	0.048399	0.036090	0.015533	0.001467

H2 1 1-SIGMA-U+ PGI 16BF (B=2P STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
-0.005853	-0.007152	-0.006710	0.000008	0.011966	0.027269	0.042740
0.015676	0.060443	0.064714	0.068115	0.049728	0.028850	0.014805
0.008806	0.131735	0.152352	0.257736	0.344744	0.400836	0.426504
0.075495	0.155797	0.163127	0.187892	0.184163	0.188063	0.211111
-0.143318	-0.220479	-0.225660	-0.209434	-0.148467	-0.052989	0.062833
0.051386	0.035583	0.034005	0.024696	0.013822	0.003216	-0.004465
0.164209	0.080318	0.075380	0.063126	0.048673	0.033105	0.020549
-0.423051	-0.355095	-0.346533	-0.300034	-0.243768	-0.180256	-0.111710
-0.048294	-0.097088	-0.106070	-0.143757	-0.161936	-0.160686	-0.144075
0.015815	-0.034495	-0.045937	-0.110255	-0.167580	-0.204026	-0.213759
-0.186281	-0.261998	-0.264394	-0.247239	-0.196353	-0.140754	-0.095576
-0.011988	-0.098686	-0.108147	-0.142770	-0.137836	-0.120066	-0.103334
0.131332	0.212837	0.219311	0.212004	0.160980	0.074387	-0.032502
-0.047417	-0.045358	-0.044707	-0.037710	-0.027475	-0.016646	-0.008136
-0.811026	-0.677907	-0.663851	-0.600691	-0.545663	-0.498526	-0.460312
-0.004434	-0.037973	-0.037874	-0.027877	-0.016195	-0.001750	0.018973

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.054615	0.064419	0.063885	0.054737	0.043876	0.023200	0.002202
0.010161	0.011852	0.011784	0.017927	0.028656	0.021167	0.005454
0.423481	0.367447	0.298923	0.190705	0.118216	0.057397	0.008768
0.245091	0.306236	0.334033	0.299168	0.165870	0.043913	0.001451
0.166554	0.252518	0.223511	0.134469	0.043363	-0.001043	0.000730
-0.007945	-0.008505	-0.008306	-0.007402	-0.003675	-0.000912	-0.000028
0.010597	-0.005157	-0.023674	-0.083428	-0.122701	-0.090895	-0.023802
-0.046533	0.037894	0.062622	0.045027	-0.023810	-0.043480	-0.012426
-0.117757	-0.058304	-0.013535	0.021128	-0.003104	-0.033853	-0.012349
-0.195558	-0.116943	-0.048020	0.010211	-0.036483	-0.093855	-0.029949
-0.069402	-0.062607	-0.079874	-0.140681	-0.167669	-0.150210	-0.039030
-0.078244	0.004246	0.088881	0.207583	0.237763	0.215187	0.053854
-0.128546	-0.197663	-0.134733	0.083381	0.320313	0.378365	0.092641
-0.003377	-0.000093	0.001200	0.001569	0.000167	-0.001379	-0.001889
-0.433935	-0.414282	-0.418702	-0.465995	-0.546924	-0.604868	-0.675465
0.041946	0.060257	0.026705	-0.107070	-0.282300	-0.365944	-0.410200

H2 2 1-SIGMA-U+ PGI 16BF (B'=3P STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	0.334933	0.316619	0.312492	0.309686	0.308663
0.0	0.0	0.330301	0.418071	0.493460	0.523632	0.521782
0.0	0.0	-0.145745	-0.117731	-0.022058	0.082439	0.179416
0.0	0.0	-0.327033	-0.246193	-0.067466	0.018720	0.028886
0.0	0.0	0.594873	0.467663	0.414881	0.306177	0.149096
0.0	0.0	0.027949	0.034425	0.035212	0.030634	0.022728
0.0	0.0	-0.058497	-0.045928	0.013334	0.055577	0.070293
0.0	0.0	0.014587	0.000620	0.002814	-0.002543	-0.021296
0.0	0.0	0.250923	0.178295	0.116944	0.072136	0.037903
0.0	0.0	0.238091	0.250687	0.204406	0.142171	0.075315
0.0	0.0	0.113856	0.090617	0.044917	0.026902	0.025925
0.0	0.0	0.377954	0.324536	0.150498	0.044720	-0.000057
0.0	0.0	-0.604769	-0.480621	-0.423793	-0.305113	-0.136870
0.0	0.0	-0.067758	-0.054314	-0.041372	-0.030233	-0.019986
0.0	0.0	-0.128599	-0.157012	-0.122119	-0.084432	-0.056758
0.0	0.0	0.073535	0.088112	0.103665	0.095634	0.061642

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.309054	0.309312	0.309057	0.308966	0.308877	0.308717	0.308319
0.510295	0.497114	0.493793	0.492991	0.493061	0.492590	0.491546
0.248442	0.298280	0.303611	0.300809	0.299382	0.299659	0.298828
0.017652	0.009852	0.014585	0.020814	0.022138	0.021589	0.022959
0.030460	-0.038015	-0.033765	-0.013653	-0.006371	-0.003093	0.000523
0.015261	0.007136	0.003970	0.001647	0.000870	0.000510	0.000060
0.068778	0.056030	0.044518	0.026446	0.015685	0.009665	0.000676
-0.036634	-0.039164	-0.030173	-0.013369	-0.005960	-0.002986	-0.000294
0.012810	-0.009189	-0.011799	-0.007710	-0.005208	-0.005587	-0.007710
0.020201	-0.025763	-0.027378	-0.013412	-0.008326	-0.008768	-0.012253
0.026914	0.018876	0.007340	-0.004036	-0.003261	-0.003033	-0.006305
-0.018454	-0.022511	-0.012843	-0.000592	-0.000750	-0.001781	-0.000589
-0.012761	0.050022	0.037244	0.010426	0.003607	0.001475	-0.000246
-0.011676	-0.003040	-0.000404	0.000349	0.000384	0.000319	-0.000045
-0.036106	-0.012445	-0.003868	0.000006	0.001345	0.002103	-0.000689
0.026328	-0.004418	-0.008994	-0.005085	-0.002966	-0.001719	0.000393

H2 2 1-SIGMA-U+ PGI 16BF (B'=3P STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	-0.044214	-0.043239	-0.026375	0.000033	0.023083
0.0	0.0	0.045527	-0.007915	-0.043078	-0.042587	-0.018029
0.0	0.0	0.834259	0.618402	0.508459	0.406121	0.287556
0.0	0.0	-0.200613	-0.236032	-0.191293	-0.029377	0.139979
0.0	0.0	-23.641495	-16.107559	-11.213413	-7.374761	-4.191580
0.0	0.0	0.027625	0.015893	0.005656	-0.001548	-0.004971
0.0	0.0	0.336358	0.228125	0.142457	0.085787	0.051646
0.0	0.0	-2.302620	-2.031122	-1.705804	-1.262699	-0.727557
0.0	0.0	-0.069512	-0.087649	-0.095881	-0.099829	-0.098266
0.0	0.0	-0.037180	-0.071595	-0.132260	-0.190825	-0.224769
0.0	0.0	-0.941424	-0.610430	-0.416956	-0.311201	-0.263449
0.0	0.0	0.340218	0.403044	0.429888	0.384673	0.335763
0.0	0.0	23.681046	16.167801	11.299436	7.500054	4.382515
0.0	0.0	-0.043480	-0.033888	-0.022642	-0.012520	-0.006168
0.0	0.0	-0.229886	-0.230099	-0.199607	-0.120363	-0.009220
0.0	0.0	-1.674272	-1.485800	-1.241198	-0.886260	-0.438212

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.032673	0.024235	0.013917	0.005700	0.003902	0.003566	0.003246
0.007103	0.020549	0.015831	0.006879	0.004158	0.004002	0.005110
0.178253	0.063385	0.027588	0.011141	0.008309	0.010479	0.012016
0.214472	0.142513	0.064741	0.015455	0.007947	0.004244	-0.009283
-1.974526	-0.401018	-0.137211	-0.025439	-0.003654	-0.001297	-0.010720
-0.005118	-0.002809	-0.001262	-0.000196	-0.000020	0.000033	0.000014
0.035014	0.025838	0.021365	0.012135	0.006724	0.005974	0.001088
-0.274108	0.036368	0.037372	0.011479	0.006724	0.005600	0.002317
-0.091567	-0.076405	-0.069481	-0.066113	-0.066882	-0.072278	-0.086318
-0.229704	-0.205761	-0.189202	-0.177612	-0.177747	-0.190647	-0.225443
-0.253544	-0.264397	-0.260231	-0.245416	-0.243291	-0.258419	-0.302804
0.335084	0.392705	0.395540	0.367327	0.360671	0.380871	0.443584
2.253496	0.850084	0.688700	0.642530	0.636778	0.676477	0.787755
-0.002923	0.000236	0.001185	0.001333	0.001234	0.001022	0.000197
0.104863	0.263828	0.341188	0.397733	0.402971	0.351266	0.063996
-0.051282	0.209926	0.220551	0.233175	0.239671	0.211162	0.039842

H2 1 3-SIGMA-G+ PGI 16BF (/A=2S STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.380650	0.334523	0.327558	0.298207	0.280256	0.273883	0.276125
0.337505	0.417561	0.430282	0.475442	0.492856	0.491677	0.480328
0.090948	0.052948	0.054306	0.071722	0.105317	0.156518	0.215211
-0.138523	-0.041470	-0.026488	0.008167	-0.001404	-0.014808	-0.024855
-0.074276	-0.060367	-0.055767	-0.047813	-0.050673	-0.038659	-0.018505
0.031544	0.040874	0.041179	0.038011	0.032800	0.026973	0.020355
-0.031328	0.005930	0.013292	0.045414	0.061607	0.068722	0.070380
0.003902	-0.023099	-0.026083	-0.041423	-0.053570	-0.056664	-0.051566
0.379269	0.274465	0.259900	0.200820	0.159057	0.127285	0.102109
-0.033259	0.119781	0.136544	0.199251	0.224503	0.212937	0.176475
-0.048601	-0.074473	-0.080309	-0.097423	-0.085808	-0.050960	-0.005271
0.119342	0.080493	0.072805	0.064744	0.077137	0.068690	0.042982
0.079132	0.050472	0.044250	0.031967	0.037664	0.034823	0.026391
-0.052852	-0.053753	-0.053519	-0.049568	-0.043388	-0.035542	-0.026576
-0.010052	-0.032521	-0.033864	-0.044207	-0.057935	-0.066082	-0.066353
-0.018046	0.006484	0.010092	0.024432	0.029795	0.031898	0.032320

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.283159	0.298076	0.305591	0.308597	0.308716	0.308281	0.308095
0.470725	0.474267	0.485063	0.491667	0.492874	0.492312	0.491247
0.264002	0.305480	0.307187	0.300094	0.295503	0.293990	0.296790
-0.027808	-0.011377	0.008354	0.023229	0.028299	0.029081	0.025353
-0.004063	-0.008831	-0.017929	-0.011559	-0.006060	-0.001461	0.002427
0.014392	0.007258	0.004032	0.001445	0.000459	0.000010	-0.000089
0.068197	0.059244	0.048626	0.030706	0.019871	0.011803	0.004653
-0.043163	-0.032377	-0.025851	-0.011865	-0.003293	0.002155	0.003685
0.081155	0.045937	0.021842	0.005212	0.004912	0.010516	0.008137
0.132461	0.062644	0.025338	0.006019	0.007164	0.016838	0.012900
0.032337	0.050714	0.032280	0.006644	0.002765	0.006963	0.007629
0.016833	-0.004976	-0.003452	0.004705	0.006853	0.006683	0.001005
0.020065	0.022742	0.021889	0.006618	0.001165	0.000560	0.001162
-0.018272	-0.007373	-0.002559	-0.000034	0.000526	0.000638	0.000231
-0.060231	-0.039274	-0.021403	-0.007619	-0.003206	0.001042	0.002172
0.030222	0.017167	0.004789	-0.001214	-0.002113	-0.003226	-0.001919

H2 1 3-SIGMA-G+ PGI 16BF (/A=2S STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
-0.039429	-0.008813	-0.005565	0.005318	0.005363	0.000668	-0.004279
-0.073511	-0.021754	-0.015275	0.005744	0.005531	0.000192	-0.002137
-0.547497	-0.436236	-0.399951	-0.249866	-0.168854	-0.122559	-0.088463
0.011480	-0.017539	0.017729	0.153510	0.136170	0.047720	-0.036807
0.297291	0.216955	0.225615	0.310398	0.373751	0.393579	0.374623
-0.051619	-0.018555	-0.016458	-0.011957	-0.010752	-0.008869	-0.006190
-0.088410	-0.123875	-0.116291	-0.060586	-0.023662	-0.009663	-0.003865
0.047346	0.040953	0.041788	0.050226	0.053347	0.048419	0.037442
-0.092125	-0.091117	-0.090440	-0.086719	-0.078463	-0.070194	-0.065158
-0.079862	-0.188997	-0.201773	-0.241881	-0.244232	-0.228610	-0.208209
0.529303	0.347786	0.302255	0.110918	-0.006499	-0.087443	-0.152801
0.694607	0.636201	0.583181	0.356507	0.287541	0.303851	0.337517
0.090291	0.312145	0.326170	0.345827	0.369328	0.414694	0.472920
-0.025829	0.010887	0.012848	0.015526	0.013861	0.010959	0.007985
0.014799	0.048998	0.067991	0.172692	0.245654	0.286891	0.313569
-0.032445	-0.047648	-0.047763	-0.035306	-0.015183	0.007505	0.034359

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
-0.007417	-0.005469	0.001801	0.008736	0.009874	0.008565	0.002396
-0.002196	0.001052	0.008645	0.015920	0.017970	0.015849	0.004748
-0.058454	-0.010084	0.011644	0.016435	0.014666	0.013104	0.000201
-0.090790	-0.099277	-0.046096	0.007789	0.014082	0.010791	0.007021
0.324038	0.185687	0.088556	0.020886	0.004259	-0.004701	-0.005657
-0.003848	-0.001680	-0.001093	-0.000838	-0.000650	-0.000462	-0.000142
0.000079	0.005563	0.005332	0.000983	0.003188	0.018938	0.017547
0.023052	-0.002202	-0.007090	0.002874	0.011466	0.018960	0.011396
-0.063058	-0.062255	-0.060002	-0.051990	-0.039537	-0.018362	0.001652
-0.191264	-0.173741	-0.163774	-0.141812	-0.107966	-0.051848	0.001809
-0.200617	-0.238424	-0.230602	-0.197898	-0.151371	-0.073980	0.000778
0.360747	0.362117	0.340816	0.297134	0.228028	0.113270	0.002022
0.535452	0.620047	0.610673	0.523111	0.399818	0.200546	0.007386
0.005667	0.002895	0.001910	0.001739	0.001815	0.001939	0.001910
0.336320	0.387765	0.441222	0.517648	0.592673	0.664134	0.680642
0.065670	0.140554	0.215183	0.297165	0.352015	0.399417	0.413095

H2 2 3-SIGMA-G+ PGI 16BF (/H=3D STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	0.315525	0.283202	0.271860	0.271110	0.0
0.0	0.0	0.355360	0.421023	0.464102	0.478465	0.0
0.0	0.0	-0.035710	0.000044	0.064382	0.131457	0.0
0.0	0.0	-0.160646	-0.126899	-0.055287	-0.016524	0.0
0.0	0.0	-0.059119	-0.057164	-0.024600	0.020236	0.0
0.0	0.0	0.043719	0.039878	0.033570	0.026665	0.0
0.0	0.0	-0.018570	0.000156	0.034123	0.056670	0.0
0.0	0.0	-0.030482	-0.046775	-0.049466	-0.041146	0.0
0.0	0.0	0.274875	0.218698	0.169807	0.131306	0.0
0.0	0.0	0.217907	0.259097	0.255833	0.224045	0.0
0.0	0.0	0.010860	-0.021053	-0.036517	-0.014771	0.0
0.0	0.0	0.206728	0.198655	0.129849	0.070647	0.0
0.0	0.0	0.048015	0.042192	0.012786	-0.022802	0.0
0.0	0.0	-0.050925	-0.047611	-0.042236	-0.034732	0.0
0.0	0.0	-0.068693	-0.092625	-0.088541	-0.080755	0.0
0.0	0.0	0.007858	0.020504	0.034576	0.047125	0.0

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.283955	0.291140	0.291126	0.297232	0.303421	0.306924	0.308269
0.466206	0.456519	0.455111	0.472538	0.484277	0.489408	0.491436
0.247771	0.283822	0.277401	0.273160	0.284614	0.294732	0.298329
0.001977	0.018192	0.038533	0.049371	0.037734	0.027382	0.023697
0.059124	0.033646	0.013093	-0.002802	0.000094	0.001210	0.000854
0.012423	0.004424	0.001104	-0.000338	-0.000380	-0.000138	0.000001
0.068580	0.061142	0.045898	0.017470	0.003114	-0.000412	0.000050
-0.017983	-0.008836	-0.004099	-0.000270	0.002301	0.001064	-0.000020
0.080206	0.069438	0.082242	0.075963	0.051725	0.027366	0.007704
0.127786	0.095723	0.114720	0.113138	0.080986	0.043648	0.012293
0.060170	0.095046	0.107557	0.076085	0.044587	0.023759	0.007171
-0.004373	-0.013504	0.001106	0.019113	0.013924	0.004938	0.000745
-0.042590	-0.019290	-0.007869	-0.000051	0.000069	0.000959	0.000170
-0.016677	-0.004925	0.000670	0.003243	0.001989	0.000807	0.000159
-0.058614	-0.034181	-0.015963	0.004021	0.008609	0.006416	0.001739
0.050319	0.030419	0.014042	-0.003910	-0.005612	-0.003233	-0.000488

H2 2 3-SIGMA-G+ PGI 16BF (/H=30 STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	0.154212	0.201907	0.198571	0.181296	0.0
0.0	0.0	0.389161	0.453733	0.408815	0.348175	0.0
0.0	0.0	0.586924	0.551571	0.377543	0.223397	0.0
0.0	0.0	1.881591	2.516232	2.415346	2.072005	0.0
0.0	0.0	0.110645	0.324155	0.596059	0.844312	0.0
0.0	0.0	0.005395	-0.003662	-0.008773	-0.010652	0.0
0.0	0.0	0.178021	0.454432	0.519531	0.457857	0.0
0.0	0.0	-3.442911	-2.495772	-1.790553	-1.216270	0.0
0.0	0.0	-0.058911	-0.098357	-0.087003	-0.061424	0.0
0.0	0.0	-0.128144	-0.156627	-0.102770	-0.049471	0.0
0.0	0.0	-0.745059	-0.776847	-0.598002	-0.381686	0.0
0.0	0.0	-1.031409	-1.324075	-1.096156	-0.753283	0.0
0.0	0.0	-0.093275	-0.616776	-1.058421	-1.414075	0.0
0.0	0.0	-0.018508	-0.021732	-0.020974	-0.018548	0.0
0.0	0.0	0.653036	0.908252	0.984455	0.970684	0.0
0.0	0.0	3.612700	2.838019	2.338111	1.990300	0.0

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.152656	0.129747	0.100465	0.040544	0.013247	0.003496	-0.000037
0.268180	0.215772	0.157878	0.052636	0.011554	-0.000072	-0.001494
0.126002	0.129856	0.085449	0.005452	-0.016066	-0.014076	-0.007252
1.396732	0.918775	0.651244	0.288362	0.135385	0.063218	0.017568
1.156084	0.986885	0.753191	0.328834	0.159406	0.072696	0.014765
-0.011775	-0.011975	-0.010360	-0.004915	-0.001906	-0.000771	-0.000158
0.294345	0.246992	0.261176	0.143958	0.052318	0.009499	-0.000586
-0.288947	0.193282	0.313605	0.158346	0.062050	0.015839	-0.000050
-0.019023	0.014662	0.044448	0.075839	0.083378	0.087276	0.087176
0.006132	0.061855	0.130207	0.203950	0.218575	0.227474	0.227307
-0.069391	0.091243	0.194484	0.262962	0.287851	0.303736	0.304855
-0.371988	-0.337749	-0.431876	-0.435597	-0.434203	-0.446650	-0.446350
-1.826891	-1.676297	-1.412466	-0.918666	-0.794206	-0.795268	-0.791904
-0.011494	-0.004148	-0.000676	0.001044	0.000888	0.000425	0.000009
0.932576	0.906746	0.868213	0.622992	0.391522	0.171299	0.011223
1.520363	1.158366	0.873568	0.438796	0.245419	0.104249	0.005689

H2 1 3-SIGMA-U+ PGI 16BF (/B=2P STATE) ORBITAL 1

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.424944	0.387512	0.381913	0.357242	0.324960	0.295066	0.273938
0.314542	0.406746	0.421026	0.477000	0.484579	0.472051	0.458064
-0.210133	-0.326652	-0.300816	-0.149719	-0.058312	0.006050	0.043456
-0.361626	-0.364294	-0.280572	0.138378	0.257015	0.221636	0.168333
0.068427	-0.098301	-0.093233	0.031106	0.067357	-0.005589	-0.102012
-0.012418	0.036372	0.039648	0.045719	0.045386	0.042116	0.037059
-0.068235	-0.087775	-0.072697	0.035129	0.092760	0.108055	0.114567
0.041179	0.004495	0.002687	0.014894	0.019534	-0.000119	-0.031438
0.307946	0.183316	0.167922	0.117131	0.110179	0.121570	0.135566
-0.007809	0.108951	0.118437	0.144247	0.173292	0.195776	0.206478
0.290270	0.411106	0.392532	0.283818	0.242846	0.235558	0.235440
0.331421	0.369421	0.289274	-0.114341	-0.225271	-0.191814	-0.146685
-0.061246	0.095169	0.089169	-0.037900	-0.073805	0.002299	0.103215
-0.091718	-0.036938	-0.030569	-0.006392	0.007228	0.013660	0.015929
0.030204	-0.024249	-0.015052	0.060004	0.093059	0.093997	0.093398
-0.014400	-0.022231	-0.020427	0.011333	0.029731	0.016653	-0.013001

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.261328	0.254874	0.262242	0.290184	0.306064	0.308418	0.308423
0.447131	0.436845	0.436072	0.464560	0.489030	0.492700	0.492093
0.112604	0.178259	0.222459	0.275372	0.290471	0.293947	0.296910
0.124969	0.075005	0.049025	0.032901	0.034269	0.031193	0.025974
-0.191952	-0.251585	-0.179085	-0.055888	-0.020527	-0.008543	-0.001190
0.031488	0.022313	0.016030	0.009279	0.006306	0.004791	0.003181
0.120657	0.121089	0.105663	0.072629	0.052544	0.039604	0.025065
-0.067956	-0.113424	-0.103245	-0.052528	-0.027272	-0.015853	-0.007333
0.146963	0.156903	0.151422	0.101886	0.069923	0.041175	0.000442
0.210926	0.215173	0.215090	0.157012	0.062796	0.017698	0.000451
0.234532	0.223936	0.193297	0.107366	0.039823	0.011144	0.001871
-0.111436	-0.065563	-0.032203	0.002096	0.002114	-0.000639	-0.002546
0.196959	0.259035	0.184362	0.054476	0.017926	0.007834	0.002843
0.016115	0.014302	0.011162	0.005125	0.001617	0.000377	-0.000077
0.096264	0.093863	0.075669	0.033352	0.009511	0.002306	0.000741
-0.049983	-0.096956	-0.087333	-0.036472	-0.013684	-0.006239	-0.002117

H2 1 3-SIGMA-U+ PGI 16BF (/B=2P STATE) ORBITAL 2

R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
-0.118929	-0.187932	-0.193892	-0.202864	-0.194685	-0.184177	-0.177245
-0.249749	-0.401498	-0.417091	-0.454106	-0.455805	-0.435488	-0.392770
-0.536380	-0.479736	-0.458956	-0.330941	-0.233759	-0.192039	-0.200827
-0.004421	0.098574	0.102636	0.081419	0.037560	0.010604	0.014658
0.955948	0.483640	0.418118	0.211987	0.109898	0.034513	-0.015463
-0.015385	-0.045890	-0.049685	-0.056728	-0.054134	-0.047721	-0.037500
-0.022893	0.037855	0.036866	0.018295	-0.004411	-0.024176	-0.036529
0.324776	0.178635	0.160454	0.105069	0.081077	0.064570	0.051972
0.011300	0.104386	0.120458	0.188135	0.232476	0.257830	0.268955
0.342246	0.436072	0.438020	0.402911	0.355809	0.335940	0.348198
0.789850	0.787784	0.770152	0.654719	0.555588	0.469666	0.381378
-0.097615	-0.216883	-0.221263	-0.202078	-0.153392	-0.097083	-0.040694
-0.936028	-0.460575	-0.394771	-0.187430	-0.087256	-0.021448	0.010318
0.065998	0.082607	0.084415	0.085637	0.078399	0.067248	0.053304
0.581450	0.344578	0.311536	0.198890	0.147111	0.123872	0.112947
-0.005931	-0.011681	-0.013370	-0.019244	-0.028083	-0.042156	-0.053119

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
-0.174980	-0.171995	-0.160159	-0.104881	-0.040634	-0.011283	-0.000429
-0.340053	-0.268951	-0.238067	-0.161428	-0.064352	-0.017877	-0.000407
-0.231822	-0.251607	-0.213360	-0.111026	-0.039095	-0.011291	-0.001999
0.033162	0.043460	0.021049	-0.008855	-0.004952	0.000585	0.002809
-0.051165	-0.075607	-0.058205	-0.025622	-0.013670	-0.007865	-0.003144
-0.025911	-0.010667	-0.004575	-0.000700	-0.000013	0.000019	-0.000095
-0.044724	-0.041512	-0.033946	-0.015853	-0.004059	-0.000541	0.000702
0.038624	0.015660	0.005233	-0.004777	-0.007356	-0.005447	-0.002294
0.270460	0.266141	0.267961	0.289566	0.304712	0.307515	0.308151
0.378645	0.421863	0.435910	0.463631	0.484755	0.489164	0.490809
0.298804	0.221226	0.227691	0.279689	0.300949	0.302508	0.300074
0.008287	0.045615	0.035000	0.012367	0.011742	0.015512	0.020890
0.027405	0.043936	0.042144	0.030933	0.019064	0.010296	0.003127
0.038768	0.019468	0.011760	0.007646	0.006082	0.004767	0.003176
0.105841	0.093269	0.082627	0.066567	0.051921	0.039640	0.025122
-0.059880	-0.063239	-0.056526	-0.038735	-0.025101	-0.015823	-0.007462

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R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	0.355168	0.304179	0.274667	0.270553	-0.277890
0.0	0.0	0.376437	0.437580	0.467813	0.476129	-0.474305
0.0	0.0	-0.128012	-0.003416	0.099548	0.169504	-0.230874
0.0	0.0	-0.181712	-0.037662	-0.018586	-0.020942	0.019204
0.0	0.0	0.164345	0.042109	-0.016871	-0.025278	0.010847
0.0	0.0	0.047717	0.045035	0.033994	0.026020	-0.018789
0.0	0.0	-0.033626	0.025620	0.054770	0.062594	-0.063507
0.0	0.0	-0.013398	-0.035222	-0.050883	-0.053849	0.046431
0.0	0.0	0.229067	0.196194	0.166228	0.130219	-0.096102
0.0	0.0	0.192052	0.239754	0.248486	0.220823	-0.167047
0.0	0.0	0.110563	-0.014160	-0.070052	-0.053913	0.015588
0.0	0.0	0.221592	0.105040	0.089446	0.071751	-0.038082
0.0	0.0	-0.175505	-0.057434	0.004443	0.021630	-0.017772
0.0	0.0	-0.043853	-0.040346	-0.040245	-0.034368	0.025601
0.0	0.0	-0.084380	-0.071191	-0.071598	-0.076683	0.073397
0.0	0.0	0.014302	0.027370	0.030878	0.032996	-0.034278

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.288741	0.303710	0.307710	0.308455	0.308409	0.308302	0.308276
0.472655	0.481256	0.488356	0.491340	0.491738	0.491658	0.491430
0.276295	0.305813	0.301966	0.296722	0.296306	0.297166	0.298547
-0.012674	0.009985	0.025142	0.030056	0.028334	0.025682	0.023300
-0.000533	-0.010712	-0.017875	-0.008439	-0.002791	-0.000178	0.001112
0.012736	0.005937	0.003203	0.001315	0.000642	0.000288	0.000029
0.060308	0.048344	0.036140	0.019402	0.010802	0.005151	0.000235
-0.036100	-0.024146	-0.018032	-0.007237	-0.002286	-0.000128	0.000229
0.065796	0.021155	0.001863	-0.005226	-0.006070	-0.006473	-0.007088
0.107589	0.024870	-0.003939	-0.009300	-0.010081	-0.013562	-0.011311
0.014781	0.022299	0.007687	-0.005143	-0.006332	-0.008954	-0.006879
0.008140	-0.011378	-0.006500	0.001911	0.002286	0.001712	-0.000164
0.013664	0.018813	0.017660	0.004940	0.001073	-0.000016	-0.000156
-0.017057	-0.006017	-0.001767	-0.000137	0.000012	-0.000114	-0.000136
-0.062197	-0.032625	-0.013670	-0.003004	-0.002236	-0.002727	-0.001676
0.031585	0.015031	0.002567	-0.001333	-0.000467	0.000158	0.000451

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R = 0.8	R = 1.4	R = 1.5	R = 2.0	R = 2.5	R = 3.0	R = 3.5
0.0	0.0	0.089436	0.059982	0.035952	0.027996	0.027215
0.0	0.0	0.230704	0.209001	0.150482	0.100415	0.065972
0.0	0.0	0.618714	0.362444	0.284907	0.242844	0.198167
0.0	0.0	-0.129785	-0.089207	-0.078968	-0.029608	0.042596
0.0	0.0	-11.412377	-6.650274	-4.587081	-3.334842	-2.333157
0.0	0.0	0.046690	0.045777	0.028633	0.016092	0.007324
0.0	0.0	0.154309	0.096469	0.059897	0.042860	0.032260
0.0	0.0	-0.898640	-0.682781	-0.556881	-0.453936	-0.334100
0.0	0.0	-0.012908	-0.037421	-0.055528	-0.064621	-0.069690
0.0	0.0	-0.179189	-0.100421	-0.095255	-0.121409	-0.153213
0.0	0.0	-0.941569	-0.670132	-0.465435	-0.337150	-0.263765
0.0	0.0	0.357572	0.405380	0.415006	0.383090	0.343408
0.0	0.0	11.417015	6.678463	4.648419	3.437741	2.495367
0.0	0.0	-0.064828	-0.060294	-0.040684	-0.025178	-0.014173
0.0	0.0	0.107823	0.197053	0.231620	0.250592	0.272622
0.0	0.0	-0.455655	-0.196137	-0.119317	-0.063616	0.023289

R = 4.0	R = 5.0	R = 6.0	R = 8.0	R = 10.0	R = 12.0	R = 16.0
0.027082	0.017923	0.006806	-0.002535	-0.004421	-0.003379	-0.000063
0.047073	0.025980	0.010326	-0.003603	-0.006600	-0.004213	0.001191
0.141751	0.050451	0.014538	-0.001566	-0.002337	0.002024	0.006609
0.105229	0.104762	0.040897	-0.009675	-0.019452	-0.023576	-0.016347
-1.454209	-0.407389	-0.134348	-0.037337	-0.020869	-0.021402	-0.013383
0.002118	-0.001082	-0.000821	0.000114	0.000391	0.000401	0.000151
0.024042	0.014887	0.012075	0.008894	0.007959	0.007588	0.001212
-0.187684	0.009155	0.028614	0.006368	0.001181	0.000483	0.000464
-0.072852	-0.074057	-0.073254	-0.074676	-0.078614	-0.083907	-0.087103
-0.176649	-0.191113	-0.191527	-0.195189	-0.205269	-0.219012	-0.227154
-0.230970	-0.233676	-0.247601	-0.259482	-0.273705	-0.292827	-0.304631
0.316962	0.334203	0.362825	0.380327	0.400757	0.428987	0.446044
1.695154	0.829972	0.684511	0.687977	0.719430	0.765045	0.791561
-0.007417	-0.001566	0.000118	0.000715	0.000710	0.000491	0.000065
0.296064	0.330057	0.343364	0.336811	0.287985	0.183884	0.016145
0.140624	0.285619	0.273758	0.225136	0.183692	0.115704	0.011110

PART 2

A Superposition Principle for Siegert Resonant States

INTRODUCTION

Since the very early days of the quantum theory of scattering, metastable states have been used to explain structure in the cross section. Nuclear scattering in particular showed many examples of sharp resonance features. Of more recent interest is the dominance of low energy electron impact spectroscopy by resonant compound states. Breit and Wigner[1] gave a very simple model formula that describes the cross section near a resonance,

$$\sigma \simeq \frac{\pi}{k^2} \frac{\Gamma^2}{(E - E_{res})^2 + \frac{1}{4}\Gamma^2} \quad , \tag{1}$$

where Γ is the width of the resonance and $1/\Gamma$ is the lifetime of the resonant state. This important one-level formula is a more than satisfactory description when the resonance widths $\{\Gamma\}$ are narrow compared with the energy separation between the resonances.

The objective here is more than just to describe the shape of the scattering cross section in terms of a simple formula such as (1). The basic idea is that the resonances are compound states of the target and projectile, that the incoming particle has some amplitude to populate each of these states, and that what is observed is the decay of these resonant states:

$$\psi_{in} \longrightarrow \underbrace{\sum_n \alpha_n \psi_n}_{\text{resonances}} + \underbrace{\psi_{out}}_{\text{unscattered.}} \tag{2}$$

$$\Big\downarrow$$

decay

The problem at hand is the characterization of the resonance energies and resonant states as manifestations of the potential, then a description of the scattering process as mediated by the resonances.

PREVIOUS APPROACHES

Kapur and Peierls[2] suggested that the eigenvalue problem,

$$-\frac{\hbar^2}{2m}\varphi_n''(r) + V(r)\varphi(r) = E_n\varphi_n(r) \qquad 0 \le r \le r_0$$
$$\varphi_n(0) = 0 \qquad \varphi_n'(r_0) = ik\varphi_n(r_0) \tag{3}$$

for a potential $V(r)$ of finite range r_0, would provide the s-wave resonance energies as eigenvalues $E_n = E_{res} + \frac{i}{2}\Gamma$. The resulting eigenfunctions $\{\varphi_n\}$ are called the Kapur-Peierls states. From these states a many-level resonance expansion formula for the cross section was derived:

$$T = \frac{\hbar^2}{2m} e^{-ikr_0} \sum_n \frac{\varphi_n^2(r_0)}{(E - E_n)N_n} - \frac{1}{k} \sin kr_0 e^{-ikr_0} , \tag{4}$$

where N_n is the normalization integral $N_n = \int_0^{r_0} \varphi_n^2(r)dr$.

This model has attracted attention for two reasons. First, it appears to offer a technique for finding the resonances for a variety of potentials, even for problems with many particles (see, for example, Ref. 3). Second, the expansion (4) over a complete[4] set of resonant states appears to provide a description of all of the structure in the scattering process in terms of the resonances.

But there is one principal difficulty. The Kapur-Peierls formula (4) predicts that the S-matrix should have poles at the Kapur-Peierls energies. Although they may in some cases be close to the actual poles, they do not coincide. The poles of the S-matrix are characteristic of the potential and hence are independent of the incoming momentum k,

whereas the Kapur-Peierls energies do depend on k. In addition, the Kapur-Peierls energies depend on the choice of r_0, even when r_0 is outside the region of the potential.

Siegert[5] noticed this difficulty and suggested an alternate eigenvalue problem:

$$-\frac{\hbar^2}{2m}\varphi_n'' + V\varphi_n = E_n\varphi_n \qquad \frac{\hbar^2}{2m}k_n^2 = E_n$$
$$\varphi_n(0) = 0, \qquad \varphi_n'(r_0) = ik_n\varphi_n(r_0)\,. \tag{5}$$

We call this the Siegert eigenvalue problem; the eigenvalues are called the Siegert energies or Siegert poles, and the eigenvectors are called the Siegert states. One can show[5] that the Siegert energies are the poles of the S-matrix, that they are independent of the actual scattering energy and the joining radius as long as it is chosen outside the actual potential, and finally that the bound states are just special solutions of the Siegert equations (5).

Siegert also provided a one-level formula that gives the correct residue of the S-matrix at the resonance-pole and reduces to the Breit-Wigner formula when the width Γ is small. But he was unable to provide a complete description of the scattering due to the lack of any many-level formula, i.e., an expansion of some kind over the resonant states. Any attempt to remedy this situation is complicated by the nonorthogonality of the Siegert states, and the rather slow convergence of the residues.

Humblet[6] in a general study of the Siegert energies found several important relations (see also Nussenzvieg,[7] Regge,[8] and Newton[9]). There are three kinds of Siegert poles, called a, b, and c. The b-poles are the bound states, with k_b along the positive imaginary axis, $k_b = i|k_b|$. The a-poles, sometimes called antibound or virtual states, lie on the negative imaginary axis, $k_a = -i|k_a|$. Some of the a-poles move up the imaginary axis and become bound states as the potential is strengthened. The c-poles are sometimes called radioactive states. They are distributed in the lower half of the complex plane, symmetrically about the imaginary axis.

Humblet showed that for potentials of finite strength and finite range there are only a finite number of a- and b-poles. The c-poles constitute a denumerably infinite set. For large n, the c-poles in the right half of the complex plane are given approximately by

$$\begin{aligned} \text{Re } k_n &= \frac{n\pi}{r_0} + 0(1/n) \\ \text{Im } k_n &= -\frac{(\sigma+2)}{2r_0} \ln n + 0(1/n) , \end{aligned} \tag{6}$$

where r_0 is the actual radius of the potential and σ is the order of the lowest term in the expansion of V(r) about $r = r_0$, $V(r) \sim (r - r_0)^{\sigma}$.

He went on to describe a Mittag-Leffler expansion of the S-matrix of the form

$$S(k) = C_m(k) + \sum_n (k/k_n)^m \frac{R_n}{k - k_n} . \tag{7}$$

The term R_n is the Siegert residue at the n^{th} pole. The value of m to

be used is arbitrary, as long as the series converges. In specific, Humblet found that it must be one or larger. The term $C_m(k)$ is supposed to be a smooth function of k, and is included to correct for the spurious $(k/k_n)^m$ dependence of the series. Although this formula (6) may be useful in deriving dispersion relations, it is less than satisfactory as a calculational device. The function $C_m(k)$ is unknown or difficult to determine. Further, the dependence on m is assuredly unphysical. We may also notice that neither Humblet's expression (7) nor that of Kapur-Peierls (4) nor even that of Breit-Wigner seem to illustrate the unitarity of the S-matrix.

With Regge[8] (see also Newton[9] and Nussenzvieg[10]) we have more hope. He examined the properties of the Jost function, which is just the coefficient of the incoming wave in the expression for the scattering wavefunction,

$$\psi_k = -\mathcal{J}(k)e^{-ikr} + \mathcal{J}(-k)e^{ikr} \tag{8}$$

(see also Ref. 9, p. 340). The S-matrix is then just

$$S = e^{2i\delta} = \frac{\mathcal{J}(-k)}{\mathcal{J}(k)} \quad . \tag{9}$$

Regge was able to show that the Jost function, and therefore the S-matrix, can be written in a Weierstrass-Hadamard infinite product over the resonances:

$$\begin{aligned} \mathcal{J}(k) &= \mathcal{J}(0)e^{ikr_0} \prod_n (1 - k/k_n) \\ S(k) &= e^{-2ikr_0} \prod_n \frac{(k_n + k)}{(k_n - k)} \quad , \end{aligned} \tag{10}$$

where r_0 is the actual radius of the potential. These products converge very slowly, but the convergence can be extrapolated (see Appendix I), and the formulas remain useful.

Regge's formula (10) gives an expansion over the resonances from the purely mathematical properties of the S-matrix, but this is not enough. In Regge's formulas we rather lose track of the physically appealing view of the resonances as transient intermediates for the scattering process.

Nussenzvieg[7, 10, 11] approached the scattering problem in nearly that way. He said that what we are really interested in is the time-evolution of the incoming wave packet ψ_{in}. If there were no potential, there would be no resonances, and ψ_{in} would become ψ_{out} with no scattering. This is described by the zero-order evolution operator $U_0(t-t')$. Nussenzvieg then defines a resonance evolution operator (or resonance propagator) for each resonance, $U_n(t-t')$. This resonance propagator describes the excitation of the resonance by ψ_{in}, and the subsequent decay. The total evolution operator is the sum of these:

$$U = U_0 + \sum_n U_n \,. \tag{11}$$

All of this led me to believe that it should be possible to use the Siegert states as a complete discrete basis for describing quantum mechanical events. In particular, I needed to develop some kind of superposition principle for Siegert states,

$$\psi_{given} = \sum_n \alpha_n \varphi_n \,. \tag{12}$$

This would presumably illustrate that once a given wavefunction is expanded over the Siegert states, any property can be written in terms of the simpler and decoupled properties of the resonant states,

$$\text{property } [\psi_{\text{given}}] \longleftarrow \text{properties } [\varphi_n] \, . \tag{13}$$

Such a superposition principle we now set out to find.

THE TWO-COMPONENT WAVEFUNCTION

We first rewrite the Siegert s-wave eigenvalue problem in a dimensionless form,

$$-\varphi'' + U\varphi = k^2\varphi \qquad \varphi(0) = 0 \qquad \varphi'(r_0) = ik\varphi(r_0)$$
$$k^2 = (2m/\hbar^2)E \qquad U = (2m/\hbar^2)V \,. \tag{14}$$

The literature of such problems with the eigenvalue in the boundary conditions is meager. However, Friedman[12] discusses two similar problems:

$$-\varphi'' = k^2\varphi \qquad \varphi(0) = 0 \qquad \varphi'(1) = k^2\varphi(1)$$
$$-\varphi'' = k^2\varphi \qquad \varphi(0) = 0 \qquad \varphi'(1) = k\,\varphi(1) \,. \tag{15}$$

A further description of these two and other related systems can be found in Appendix II.

The important result of the work shown in Appendix II is that we consider writing the solutions to Eq. (14) as two-component wavefunctions,

$$\Phi_n = \begin{bmatrix} \varphi_n^{(1)}(r) \\ \varphi_n^{(2)}(r) \end{bmatrix} . \tag{16}$$

Then the eigenvalue problem is rewritten as

$$L\Phi_n = \begin{bmatrix} \varphi_n^{(2)\prime}(r) \\ \varphi_n^{(1)\prime}(r) + \int_r^{r_0} U(x)\varphi_n^{(1)}(x)dx \end{bmatrix} = ik_n\Phi_n \,, \tag{17a}$$

with the boundary conditions

$$\varphi_n^{(1)}(0) = 0, \qquad \varphi_n^{(1)}(r_o) = \varphi_n^{(2)}(r_o). \tag{17b}$$

The upper component $\varphi_n^{(1)}(r)$ from a solution Φ_n of Eq. (17) can be seen to be a solution to (14) by differentiation of the lower components of (17a):

$$\varphi_n^{(1)''} - U\varphi_n^{(1)} = ik_n\varphi_n^{(2)'} = -k_n^2\varphi_n^{(1)} . \tag{18}$$

In this two-component space we define the inner product by

$$\langle \Psi, \Phi \rangle = \int_0^{r_o} [\psi^{(1)}\varphi^{(1)} - \psi^{(2)}\varphi^{(2)}] \tag{19}$$

where

$$\Psi = \begin{bmatrix} \psi^{(1)} \\ \psi^{(2)} \end{bmatrix} \qquad \Phi = \begin{bmatrix} \varphi^{(1)} \\ \varphi^{(2)} \end{bmatrix} .$$

With the boundary conditions (17b) and the inner product (19) we can find the adjoint operator L^+:

$$L^+\Phi = \begin{bmatrix} \varphi^{(2)'}(r) - U(r) \int_0^r \varphi^{(2)}(x)dx \\ \varphi^{(1)'} \end{bmatrix} \tag{20}$$

This defines a new set of adjoint eigenvectors (with the old eigenvalues)

$$L^+\Phi_n^+ = ik_n\Phi_n^+ . \tag{21}$$

We notice further that if the boundary conditions (17b) are satisfied, then

$$L^2\Phi_n = \begin{bmatrix} \varphi_n^{(1)''} - U\varphi_n^{(1)} \\ \varphi_n^{(2)''} + \int_r^{r_0} U(x)\varphi_n^{(2)'}(x)dx \end{bmatrix} = -k_n^2 \Phi_n$$

$$L^{+2}\Phi_n^+ = \begin{bmatrix} \varphi_n^{+(1)''} - U\varphi_n^{+(1)} \\ \varphi_n^{+(2)''} - U\varphi_n^{+(2)} - U'(r)\int_0^r \varphi_n^{+(2)} \end{bmatrix} = -k_n^2 \Phi_n^+ \ . \tag{22}$$

Equations (17), (20), and (22) show that the upper components of $\{\Phi_n\}$ and $\{\Phi_n^+\}$ can be chosen to be the same and that this function, $\varphi_n = \varphi_n^{(1)} = \varphi_n^{+(1)}$, is the physical Siegert resonant wavefunction. The lower components are yet without physical interpretation.

Toward the goal of a superposition principle, it will be necessary to evaluate the inner product of Φ_n^+ with Φ_ℓ. The choice of the form of the inner product and the relation of L^+ to L make this especially simple. The two vectors obey

$$L\Phi_\ell - ik_\ell\Phi_\ell = 0 \tag{23a}$$

$$L^+\Phi_n^+ - ik_n\Phi_n^+ = 0 \ . \tag{23b}$$

Taking the inner product of Φ_n^+ with Eq. (23a) and Φ_ℓ with (23b) and subtracting yields

$$\begin{aligned} i(k_n - k_\ell)\langle \Phi_n^+, \Phi_\ell \rangle &= \langle L^+\Phi_n^+, \Phi_\ell \rangle - \langle \Phi_n^+, L\Phi_\ell \rangle \\ &= \langle \Phi_n^+, L\Phi_\ell \rangle - \langle \Phi_n^+, L\Phi_\ell \rangle \\ &= 0 \ . \end{aligned} \tag{24}$$

So that either $\langle \Phi_n^+, \Phi_\ell \rangle = 0$, or $k_\ell = k_n$. The solutions are in general nondegenerate,[7] so we have

$$\langle \Phi_n^+, \Phi_\ell \rangle = N_\ell \delta_{n\ell} \ , \tag{24'}$$

where $\delta_{n\ell}$ is the Kronecker delta and N_ℓ may be considered the (not necessarily real) norm of the state. As is customary in quantum mechanics, the normalization constant could be absorbed in to the wavefunction, yielding $N_\ell = 1$, except that a Siegert state could possibly have a norm of zero. This is because the "norm" calculated from the inner product is not positive definite.

Now we have our superposition principle. To expand a given two-component vector

$$F = \begin{bmatrix} f^{(1)} \\ f^{(2)} \end{bmatrix} \longrightarrow \sum_n \alpha_n \Phi_n \ , \tag{25}$$

we only need to calculate

$$\alpha_\ell = \frac{1}{N_\ell} \langle \Phi_\ell^+, F \rangle = \frac{1}{N_\ell} \int_0^R [\, \varphi_\ell^{+(1)} f^{(1)} - \varphi_\ell^{+(2)} f^{(2)} \,]. \tag{26}$$

EXPANSION OF THE PHYSICAL SCATTERING STATE

For any energy there exists a function ψ_k satisfying

$$-\psi_k'' + U\psi_k = k^2\psi_k, \qquad \psi_k(0) = 0. \tag{27}$$

This (ψ_k) is the exact scattering wavefunction. The principal goal of this work is to find a set of coefficients $\alpha_\ell(k)$ such that

$$\psi_k(r) = \sum_n \alpha_n(k)\,\varphi_n(r); \tag{28}$$

that is, to express ψ_k as a superposition of Siegert resonances.

The function ψ_k gives only the upper component of the vector to be expanded:

$$\Psi_k = \begin{bmatrix} \psi_k \\ ? \end{bmatrix} = \sum_n \alpha_n(k)\Phi_n\,. \tag{29}$$

At this point it does not seem too important what lower component is used. Physically, we are only interested in the upper component, at least for now. There are two difficulties. First, even though the upper component of Ψ_k seems independent of the lower one, the expansion coefficients will depend on both components through Eq. (26). This is the same as saying that there are many sequences of coefficients $\{\alpha_n\}$ that give the same expanded upper component. The series (28) will not converge at all if the lower component is poorly chosen. Poor convergence results from a mediocre choice. Second, the expansion (28) will be essentially a waste of time if we actually have to evaluate integrals involving ψ_k. If the Siegert states are really a natural basis for the

scattering problem, the stationary wavefunction, ψ_k, whould be expressable directly. That is what Kapur and Peierls did.

A little experimentation with Fourier series convinces one that the attempt to expand a function that does not satisfy the same boundary conditions as the basis set produces slow and nonuniform convergence (see also Appendix II). The problem is at its worst when expanding in Siegert states. The Siegert states, even when normalized to unity [see Eq. (24)] are not bounded with respect to k_n. The point in the interval at which convergence will be the most difficult to obtain will be $r = r_0$, since there the Siegert states will in general be the largest.

It was found (see also Appendix II) that an expansion over Siegert states [Eq. (25)] will not converge at all unless at least three conditions are met,

$$\begin{aligned} &1) \quad f^{(1)}(0) = 0 \\ &2) \quad f^{(1)}(r_0) = f^{(2)}(r_0) \\ &3) \quad f^{(1)'}(r_0) = f^{(2)'}(r_0) \, . \end{aligned} \tag{30}$$

For the problem at hand, the expansion of the physical state ψ_k, the lower component of Ψ_k, which we have complete freedom to specify, is uniquely defined if Ψ_k is required to satisfy the very useful relation

$$L^2 \Psi_k = -k^2 \Psi_k \, . \tag{31}$$

This equation is a relatively natural choice since its upper component is identical to Eq. (27).

All of this gives

$$\Psi_k = \begin{bmatrix} \psi_k \\ a\int^x \psi_k + b\int^x \bar{\psi}_k + c \end{bmatrix} \tag{32}$$

where $\bar{\psi}_k''$ satisfies

$$-\bar{\psi}_k'' + U\bar{\psi}_k = k^2\bar{\psi}_k\,, \qquad \bar{\psi}'(0) = 0, \tag{33}$$

and a, b, and c are constants to be determined. Having chosen Ψ_k we need only evaluate

$$\alpha_n(k) = 1/N_n \langle \Phi_n^+, \Psi_k \rangle\ . \tag{34}$$

To evaluate α_n we use a trick much like that used by Kapur and Peierls: From (21) we have

$$\Phi_n^+ = \frac{L^{+2} + k^2}{(ik_n)^2 + k^2}\Phi_n^+\ , \tag{35}$$

so that

$$\alpha_n = \frac{1}{(k^2 - k_n^2)N_n}\left\{k^2\langle \Phi_n^+, \Psi_k\rangle + \langle L^{+2}\Phi_n^+, \Psi_k\rangle\right\}\ . \tag{36}$$

But now

$$\langle L^{+2}\Phi_n^+, \Psi_k\rangle = \langle L^+\Phi_n^+, L\Psi_k\rangle - \left[[L^+\Phi_n^+]^{(1)}\psi_k^{(2)} - [L^+\Phi_n]^{(2)}\psi_k^{(1)}\right]_0^{r_0}$$

$$= \langle L^+\Phi_n^+, L\Psi_k\rangle + 0\ . \tag{37a}$$

Next

$$\langle L^+\Phi_n^+, L\Psi_k\rangle = \langle \Phi_n^+, L^2\Psi_k\rangle - \left[\varphi_n^{+(1)}[L\Psi_k]^{(2)} - \varphi_n^{+(2)}[L\Psi_k]^{(1)}\right]_0^{r_0}$$

$$= \langle \Phi_n^+, L^2\Psi_k\rangle - b\,\bar{\psi}_k(0)\varphi_n^{+(2)}(0)\ . \tag{37b}$$

Finally, using (36) and (31)

$$\alpha_n(k) = \frac{-b\,\bar{\psi}_k(0)\,\varphi_n^{+(2)}(0)}{(k^2 - k_n^2)N_n} = \frac{-b\,\psi_k(0)\,\varphi_n'(0)}{(k^2 - k_n^2)N_n(-ik_n)} \quad . \tag{38}$$

Now the term $-b\bar{\psi}_k(0)$ is unknown until after we have solved for the exact scattering wavefunction. But it is independent of n, so it will be replaced by A(k) and treated as a normalization constant to be determined later (or even ignored). So that the expansion formula is

$$\psi_k(r) = A(k)\sum_n \frac{1}{(k^2 - k_n^2)} \frac{\varphi_n'(0)}{(-ik_n)N_n} \varphi_n(r) \; . \tag{39}$$

Let us stop and analyze this formula. It specifies how the plane-wave-like stationary state ψ_k is to be expanded over the Siegert resonant states φ_n. Aside from the common normalization factor A(k), the coefficients have a very simple dependence on k

$$\alpha_n(k) \sim \frac{1}{k^2 - k_n^2} \quad . \tag{40}$$

We note as well that the nonphysical lower components of both Ψ_k and Φ_n have disappeared from the formula. Having this principle of superposition, we now proceed to calculate the best known property of ψ_k, the phase shift.

THE PHASE SHIFT

According to Wu and Ohmura (page 64 of Ref. 13), if the exact scattering wavefunction is normalized such that

$$\psi_k(r) = \sin kr + \tan\delta \cos kr \qquad \text{for} \qquad r \geq r_0 \,, \tag{41}$$

then ψ_k satisfies the Lippman-Schwinger equation

$$\psi_k(r) = \sin kr - \int_0^r G(r, r')U(r')\,\psi_k(r')dr' \,. \tag{42}$$

Comparing (39) and (42) for $r = r_0$, we get

$$\begin{aligned} A(k) \sum_n \frac{\beta_n}{k^2 - k_n^2}\,\varphi_n(r_0) &= \sin kr_0 \\ - A(k)\,\frac{\cos kr_0}{k} \sum_n \frac{\beta_n}{k^2 - k_n^2} \int_0^{r_0} &\sin kr'\, U(r')\,\varphi_n(r')dr' \,, \end{aligned} \tag{43}$$

where

$$\beta = \varphi_n'(0)/(-ik_nN_n) \,.$$

The uniform convergence of Eq. (39) has been assumed. Equation (43) provides the value of A(k).

Finally we solve for the phase shift

$$\operatorname{ctn}\delta = \frac{-k \sum_n \frac{\beta_n}{k^2 - k_n^2}\,\varphi_n(r_0)}{\sin kr_0 \sum_n \frac{\beta_n}{k^2 - k_n^2} \int_0^{r_0} \sin kr'\, U(r')\,\varphi_n(r')\,\varphi_n(r')dr'} - \operatorname{ctn} kr_0 \tag{44}$$

and the S-matrix

$$S = e^{2i\delta} = \frac{\operatorname{ctn}\delta + i}{\operatorname{ctn}\delta - i} \,.$$

THE SQUARE WELL

The above description of the scattering process is not an attempt to give yet another dispersion formula. It was hoped that the Siegert states would provide a practical, discrete (to a good approximation finite), and calculable basis with which to describe scattering events. On this line it is necessary to consider an example. In fact, the example has been the fulcrum of the theory.

Specifically we consider

$$U(r) = \begin{cases} -\frac{1}{2} & 0 \le r \le r_0 = 1 \\ 0 & r > r_0 \end{cases} \tag{45}$$

This is a rather weak potential; the resonances are far from the real axis; and therefore the theory should be hard pressed. The Siegert states are

$$\Phi_n = \begin{bmatrix} \sin k'_n r \\ -i \dfrac{k_n}{k'_n} \cos k'_n r + i\left(\dfrac{k_n}{k'_n} - \dfrac{k'_n}{k_n} \right) \cos k'_n \end{bmatrix} \tag{46a}$$

$$\Phi_n^+ = \begin{bmatrix} \sin k'_n r \\ -i \dfrac{k'_n}{k_n} \cos k'_n r \end{bmatrix} \tag{46b}$$

where $k'^2_n = k_n^2 - U = k_n^2 + \frac{1}{2}$. The resonance eigenvalues satisfy [from Eq. (17b)]

$$k'_n \cos k'_n = ik_n \sin k'_n , \tag{47}$$

which can be solved by Newton's method or as in Ref. 7.

A few of the calculated Siegert resonance eigenvalues are given in Table I.

TABLE I. Some Siegert S-wave eigenvalues for the finite square well depth $U = -\frac{1}{2}$, radius $r_0 = 1$.

n[a]	Re k_n	Im k_n	Re k'_n	Im k'_n
0	0.0	-1.6506	0.0	-1.4914
1	4.0993	-2.6555	4.1423	-2.6279
2	7.4268	-3.1404	7.4553	-3.1284
3	10.661	-3.4642	10.682	-3.4573
4.	13.859	-3.7083	13.876	-3.7038
5.	17.040	-3.9044	17.054	-3.9012
6	20.210	-4.0684	20.222	-4.0660
7	23.373	-4.2094	23.384	-4.2075

[a] The corresponding resonances with $n < 0$ satisfy $k_n = -k^*_{-n}$.

Figure 1 shows these eigenvalues plotted in the complex k plane. The x's are the Siegert eigenvalues (poles of the S-matrix), the O's are the negatives of these (the zeros of the S-matrix).

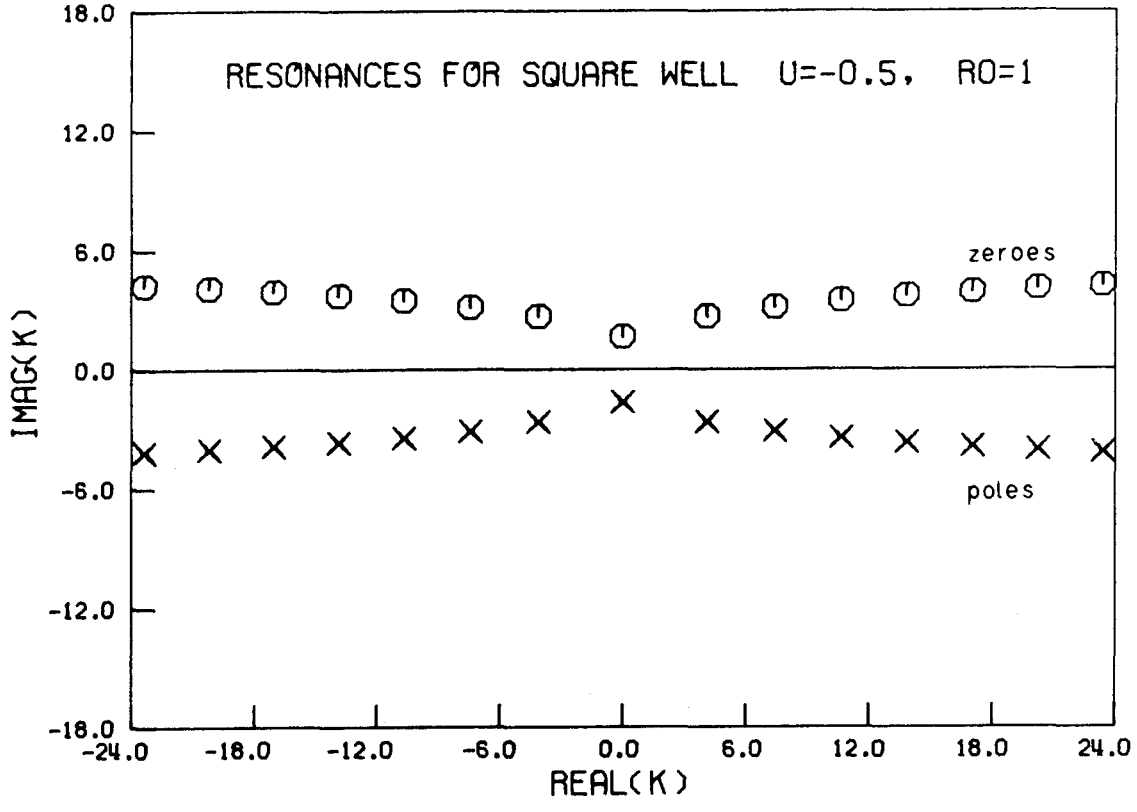

Fig.1 Siegert poles.

In Fig. 2 we see plots of the real and imaginary parts of $\varphi_n^{(1)}(r)$ and $\varphi_n^{(2)}$ for some of the first few resonances.

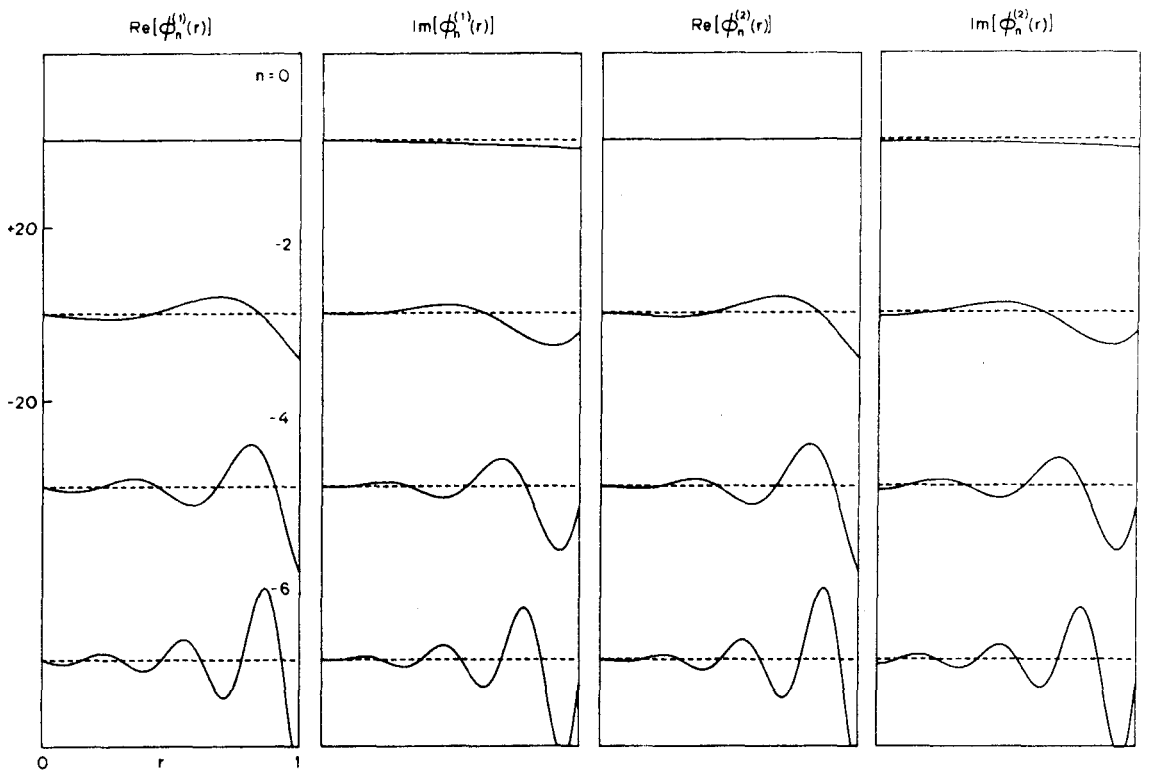

Fig. 2 Siegert resonant states for a square well.

To accomplish the expansion as in Eq. (37), we will need to know the norm, $N_n = \langle \Phi_n^+, \Phi_n \rangle = 1 + i/k_n$, and $\varphi_n'(0) = k_n'$. So

$$\psi_k(r) = A(k) \sum_n \frac{1}{k^2 - k_n^2} \frac{k_n'}{ik_n(1+i/k_n)} \sin k_n' r . \tag{48}$$

Comparisons of partial expansions of this uniformly convergent series with the known wavefunctions are shown in Figs. 3 and 4. The correct value of A(k) was used in each case.

As a final illustration, we have in Fig. 5 plots of the phase shift, δ_0, calculated from Eqs. (48) and (44) along with the cross section, $\sigma_0 = \pi/k^2 \sin^2 \delta_0$, for various numbers of expansion terms. The exact result is shown for comparison. We note the excellent agreement.

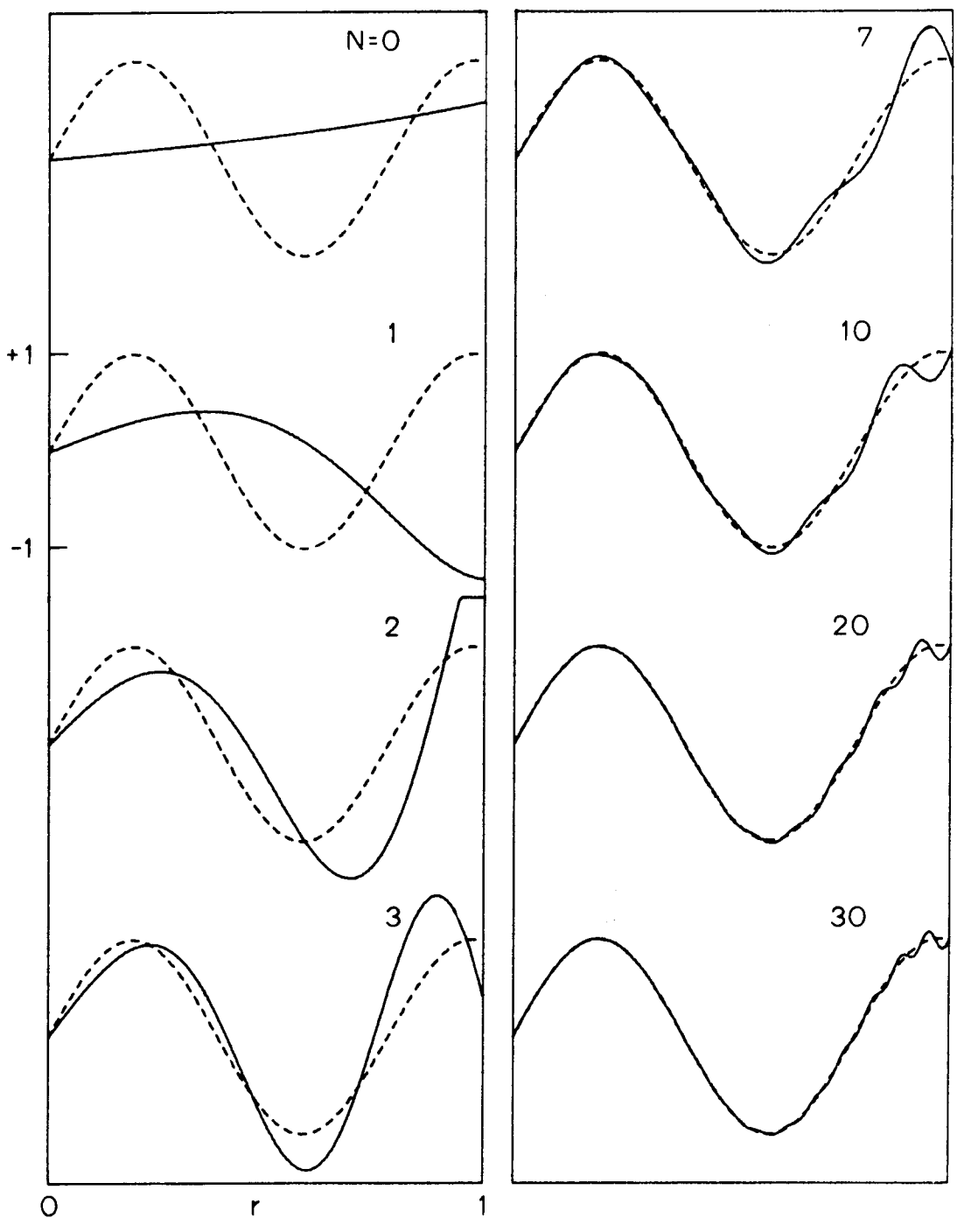

Fig.3 Expansion $\psi_k(r)=\sum_{-N}^{N}\alpha_n\phi_n(r)$ over square well Siegert states for $k=8$.

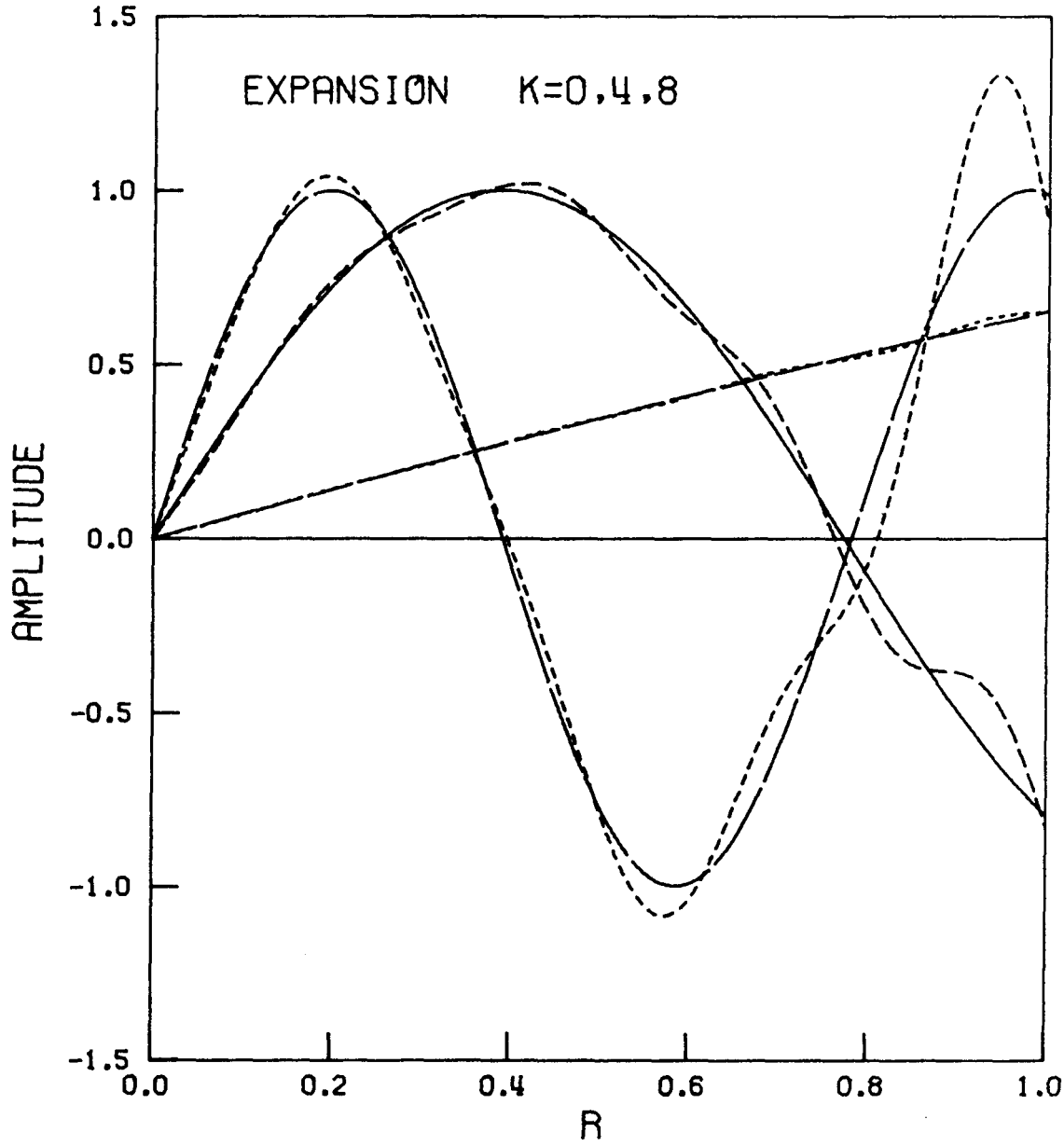

Fig.4 Siegert expansion to n=±6.

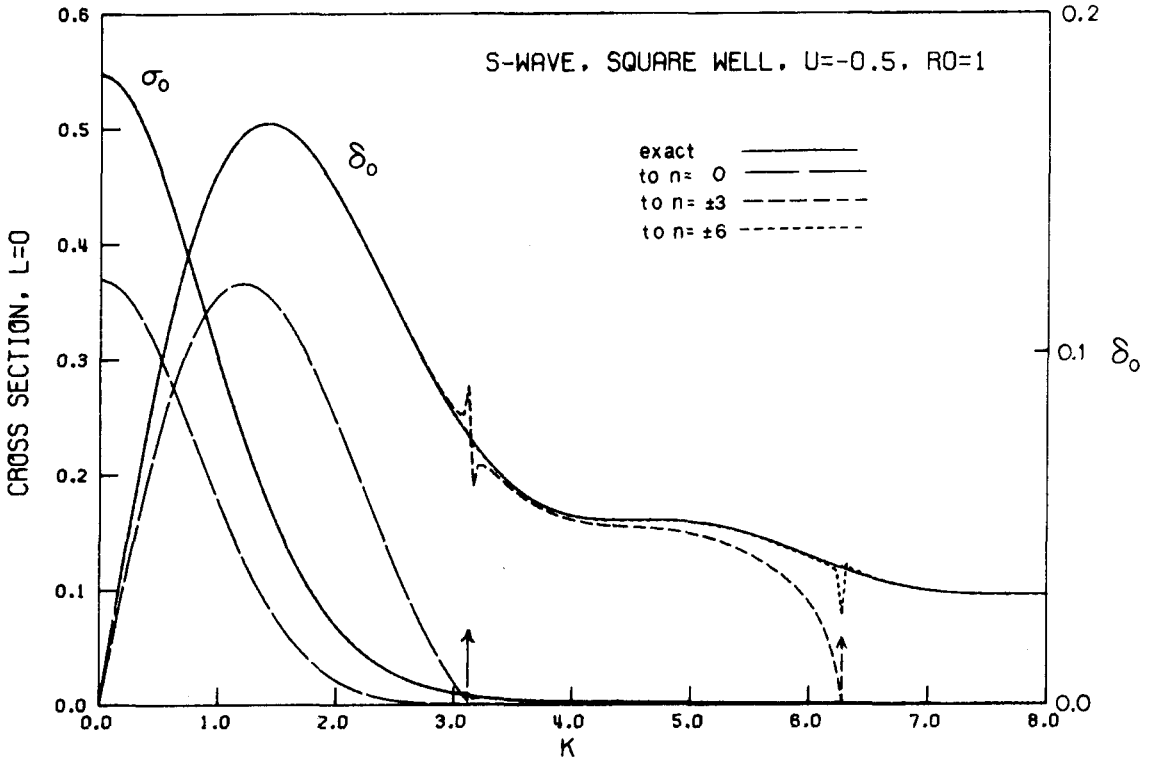

Fig.5 Siegert expansion of δ_0 and σ_0.

CONCLUSION

This chapter has discussed a uniformly convergent expansion of the scattering wavefunction over the Siegert resonant states. This is not to be viewed as the derivation of a dispersion formula but rather as the beginning of a calculational device. If the Siegert states turn out to resemble the bound states as much as it now appears that they do, then all of the powerful and successful techniques that have been used in bound state quantum mechanics may then be used for scattering states. The scattering problem is just an expansion over the bound-like Siegert states.

The sense of accomplishment that might be expected must be deflated by one important observation. All of the results of this chapter apply, as yet, only to potentials of finite range (dying faster than any exponential). No physical problem has a potential of such short range. But resonances are still observed. The experience gained in this research indicates (to me at least) that the work now in progress on Siegert states for long-range potentials will bring very similar results. At that point the theory will have come to the motivation: electron-molecule scattering.

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APPENDIX I

The Regge Formula

An unfortunate difficulty with some formal expressions in theoretical physics is the failure of these expressions to survive even simple test cases. Such is almost true of Regge's expansion formula[1, 2]

$$\mathcal{J}(k) = \mathcal{J}(0)\, e^{ikr_0} \prod_n (1 - k/k_n) \,. \tag{1}$$

For the simple case of the square well (see also the last part of the preceding chapter) it took considerable strain to make it work. Even after fifty terms it showed no threat of converging, and in specific not to the correct answer, which is

$$\begin{aligned} \mathcal{J}(k) &= e^{ikr_0}[\cos k' r_0 - ik/k' \sin k' r_0] \\ k' &= \sqrt{k^2 - U} \quad . \end{aligned} \tag{2}$$

So I went back a few steps: basically the product

$$\mathcal{J}(k) = \mathcal{J}(0)\, e^{ick} \prod_n (1 - k/k_n)\, e^{k/k_n} \tag{3}$$

converges beautifully. The constant c can be seen to be the scattering length from the logarithmic derivative

$$\begin{aligned} \frac{\dot{\mathcal{J}}(k)}{\mathcal{J}(k)} &= ic + \sum_n \left[\frac{1}{k_n} - \frac{1}{k_n(1 - k/k_n)} \right] \\ &= ic + \sum_n \left[\frac{1}{k_n} - \frac{1}{k_n - k} \right] \,, \end{aligned} \tag{4}$$

so that

$$\frac{\mathcal{J}(0)}{\mathcal{J}(0)} = i\dot{\delta}(0) = ic \ . \tag{5}$$

What happened is that Regge rearranged Eq. (3) into Eq. (1) by using the relation (which he proved) that

$$r_0 = c - i \sum_n 1/k_n \ . \tag{6}$$

The cause of the slow convergence of (1) is the slow convergence of (6). The convergence of (6) can be accelerated, and hence c calculated from r_0, by an extrapolation as follows.

Due to the symmetric placement of the poles about the imaginary axis (that is, $-k_n^*$ is a pole if k_n is), we find that

$$i \sum_n 1/k_n = - \sum \mathrm{Im}(1/k_n) = \sum \frac{\mathrm{Im}(k_n)}{|k_n|^2} \ . \tag{7}$$

Using Eq. (5) of the preceding chapter, we approximate for large n,

$$\frac{\mathrm{Im}(k_n)}{|k_n|^2} \simeq \frac{\mathrm{Im}(k_n)}{[\mathrm{Re}(k_n)]^2} \simeq A \frac{\ell n \ n}{n^2} \ . \tag{8}$$

Now having summed the first m terms

$$\sum_{n=-m}^{m} \frac{\mathrm{Im}(k_n)}{|k_n|^2} \ , \text{ the remainder } \sum_{n=m+1}^{\infty} \frac{2\mathrm{Im}(k_n)}{|k_n|^2}$$

can be estimated through the relation

$$\int_{m+2}^{\infty} \frac{\ell n \ y}{y^2} dy \leqslant \sum_{n=m+1}^{\infty} \frac{\ell n \ n}{n^2} \leqslant \int_{m+1}^{\infty} \frac{\ell n \ y}{y^2} dy \ . \tag{9}$$

When this is done, the scattering length can be calculated through

Eq. (6) to an accuracy of about three decimal places using about twenty resonance pairs $(k_n, -k_n^+)$. The total error in c is then about the size of the last term included.

The conclusion is that Regge's expansion can be a practical calculational device provided it is used in the form specified in Eq. (3) and that the scattering length must be calculated in advance.

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1. T. Regge, Nuovo Cimento 8, 671 (1958).

2. R. G. Newton, Scattering Theory of Waves and Particles (McGraw-Hill Book Co., Inc., New York, 1966); see especially Secs. 12.1.2, 12.1.3, and 12.1.4.

APPENDIX II

Eigenvalue Problems Similar to Siegert's.

This Appendix contains a brief description of a progression of eigenvalue problems culminating in that of Siegert. Of special concern will be the convergence of expansions over the eigenvectors from these systems.

A. The first problem (mostly from Friedman, [1] pp. 205-207) is

$$-\varphi'' = k^2\varphi, \qquad \varphi(0) = 0, \qquad \varphi'(1) = k^2\varphi(1). \tag{1}$$

The solution is written in the form

$$\Phi = \begin{bmatrix} \varphi(x) \\ \varphi_1 \end{bmatrix} = \begin{bmatrix} \sin k_n x \\ \sin k_n \end{bmatrix} \tag{2}$$

with the boundary conditions $\varphi(0) = 0$, $\varphi(1) = \varphi_1$. The eigenvalue equation is then

$$L\Phi_n = \begin{bmatrix} -\varphi_n''(x) \\ \varphi_n'(1) \end{bmatrix} = k^2\Phi_n \tag{3}$$

The inner product is

$$[\Phi, \Psi] = \int_0^1 \varphi(x)\,\psi(x) + \varphi_1\psi_1 . \tag{4}$$

The eigenvalues to this self-adjoint problem are given by $\mathrm{ctn}(k) = k$.

To expand a given vector

$$F = \begin{bmatrix} f(x) \\ f_1 \end{bmatrix} \rightarrow \sum_n \alpha_n\Phi_n , \tag{5}$$

we take

$$\alpha_n = \frac{[\Phi_n, F]}{[\Phi_n, \Phi_n]} = \frac{\int_0^1 \sin k_n x f(x) + \sin k_n f_1}{[1 + \sin^2 k_n]/2} . \tag{6}$$

We may ask: if the same f(x) will be obtained in the expansion (5) for every value of f_1, what effect does f_1 have? Alternately, if we know f(x), how should we choose f? These questions can be answered by the following:

1) Consider some finite series $\sum_n^N \alpha_n \Phi_n$. Now since $\varphi_n(1) = \varphi_{n,1}$ for each n, then $\sum_n^N \alpha_n \varphi_n(1) = \sum_n^N \alpha_n \varphi_{n,1}$, as well as $\lim_{N\to\infty} \sum_n^N \alpha_n \varphi_n(1) = \lim_{N\to\infty} \sum_n^N \alpha_n \varphi_{n,1}$ (if they converge at all). But now $\sum_n^N \alpha_n \varphi_{n,1} = f_1$, so that if $f(1) \neq f_1$ the $\sum_n \alpha_n \varphi_n(x)$ will not converge to f(x) at x = 1. This nonuniform convergence near x = 1 means slower convergence on the rest of the interval. This problem is illustrated by a comparison of the expansions of $F = \begin{bmatrix} x \\ 0 \end{bmatrix}$ and $G = \begin{bmatrix} x \\ 1 \end{bmatrix}$ in Figs. 1a and 1b.

2) Next consider expanding a vector of the form $H = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$. The formula (6) gives

$$\alpha_n = \frac{\sin k_n}{[1 + \sin^2 k_n]/2} . \tag{7}$$

A plot of the expansion $\sum_n \alpha_n \varphi_n(x)$ is shown in Fig. 1c. This almost-everywhere-zero (called null) expansion is what is causing the convergence difficulty shown in Fig. 1a,

$$\begin{bmatrix} x \\ 0 \end{bmatrix} = \begin{bmatrix} x \\ 1 \end{bmatrix} - \begin{bmatrix} 0 \\ 1 \end{bmatrix} , \tag{8}$$

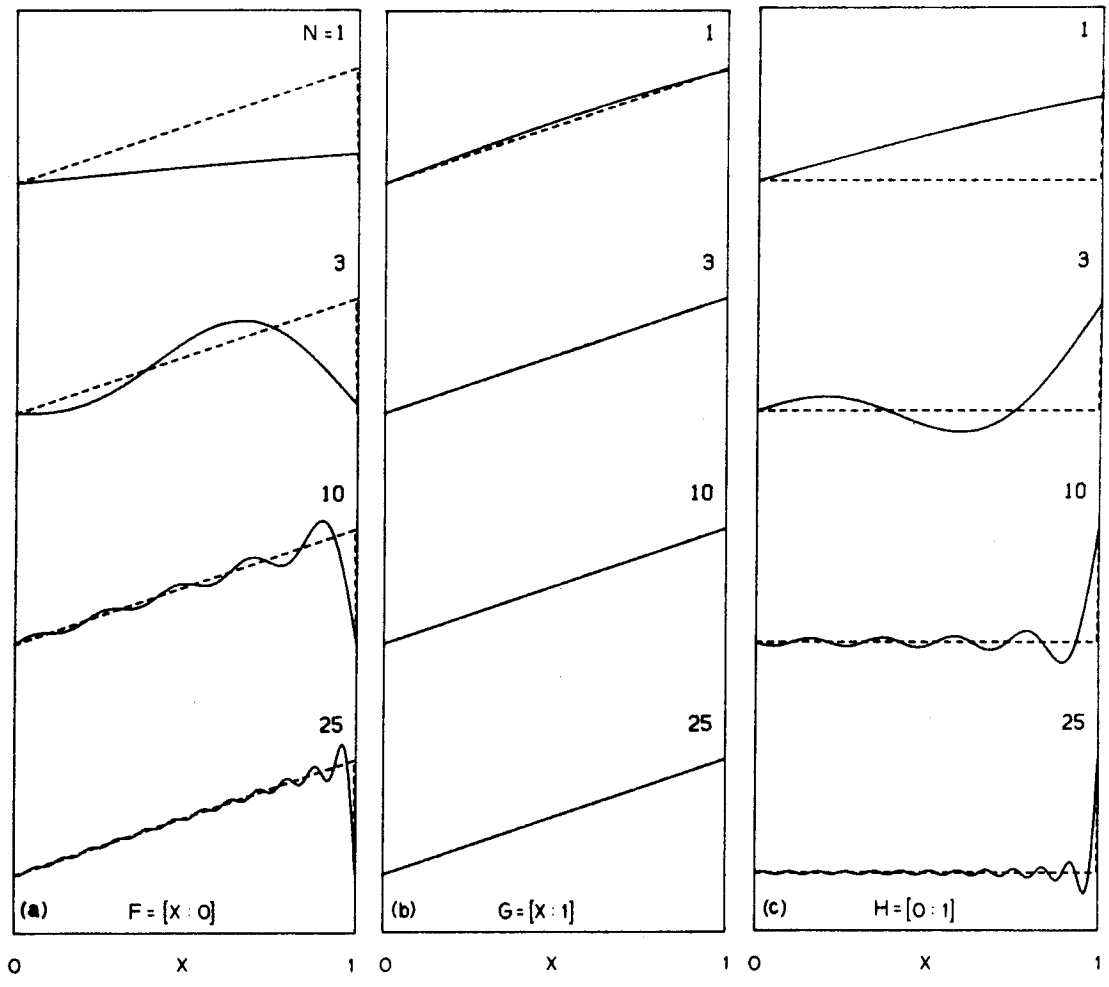


Fig. 1

$$\sum_{n}^{N} \alpha_n \sin(k_n x) \qquad \mathrm{ctn}(k_n) = k_n$$

so that all we can do to get rapid convergence is to make sure that the null expansion is eliminated. This is done by choosing $f_1 = f(1)$.

B. The second problem is the same as the first except that there is a potential:

$$-\varphi''(x) + U(x)\,\varphi(x) = k^2\,\varphi(x)\,, \qquad \varphi(0) = 0, \qquad \varphi'(1) = k^2\varphi(1)\,. \tag{9}$$

The same two-component form for the solution

$$\Phi = \begin{bmatrix} \varphi(x) \\ \varphi_1 \end{bmatrix} \tag{10}$$

with the same boundary conditions and inner product. The operator is different, of course,

$$L\Phi_n = \begin{bmatrix} -\varphi_n'' + U\varphi_n \\ \varphi_n'(1) \end{bmatrix} = k^2\Phi_n \quad . \tag{11}$$

The problem is self-adjoint (for real U) and for $U(x) = U_0$. The eigenvalues are given by $k' \operatorname{ctn} k' = k^2$, $k' = \sqrt{k^2 - U}$. Expansions are to be done in the same way as in Sec. A: the same convergence difficulties arise; no examples will be given.

C. The third problem discussed here (the second of Friedman) is much like the first but with a different right-hand boundary condition,

$$-\varphi'' = k^2\varphi\,, \qquad \varphi(0) = 0, \qquad \varphi'(1) = k\,\varphi(1)\,. \tag{12}$$

This time the two-component solution is made from two functions,

$$\Phi_n = \begin{bmatrix} \varphi_n^{(1)}(x) \\ \varphi_n^{(2)}(x) \end{bmatrix} \tag{13}$$

The boundary conditions are $\varphi_n^{(1)}(0) = 0$, $\varphi_n^{(1)}(1) = -\varphi_n^{(2)}(1)$. The eigenvalue equation is then written (following Friedman)

$$L\Phi_n = \begin{bmatrix} \varphi_n^{(2)\prime} \\ -\varphi_n^{(1)\prime} \end{bmatrix} = k\,\Phi_n \,. \tag{14}$$

From this equation we see that $\varphi_n^{(1)}$ is a solution to the original eigenvalue problem (12). A little experimentation shows that the inner product

$$\{\Phi, \Psi\} = \int_0^1 [\,\varphi^{(1)}\psi^{(1)} + \varphi^{(2)}\psi^{(2)}\,] \tag{15}$$

makes the eigenvalue problem (14) self-adjoint. The eigenvalues are given by ctn k = 1 or $k = (n + \frac{1}{4})\pi$, $n = 0, \pm 1, \pm 2, \cdots$.

To expand a given vector,

$$F = \begin{bmatrix} f^{(1)}(x) \\ f^{(2)}(x) \end{bmatrix} \rightarrow \sum_n \alpha_n \Phi_n \tag{16}$$

we take

$$\alpha_n = \frac{\{\Phi_n, F\}}{\{\Phi_n, \Phi_n\}} = \int_0^1 [\,\varphi_n^{(1)} f^{(1)} + \varphi_n^{(2)} f^{(2)}\,] \,, \tag{17}$$

where the eigenfunction has been chosen such that $\varphi_n^{(1)} = \sin k_n x$, $\varphi_n^{(2)} = -\cos k_n x$, so that $\{\Phi_n, \Phi_n\} = 1$. Once again, given the function $f^{(1)}(x)$, the $f^{(2)}(x)$ that should be used is not apparent. This time there is just one number to be determined but a <u>function</u> over the entire interval $[0, 1]$. There are now many "null" functions $\begin{bmatrix} 0 \\ f^{(2)}(x) \end{bmatrix}$.

An attack on this difficulty can be made by looking at other eigenvalue problems with the same eigenvectors. The first of these is

$$-\varphi'' = k^2 \varphi, \qquad \varphi(0) = 0, \qquad \varphi'(2) = 0, \tag{18}$$

whose space of eigensolutions is the same as that made from those solutions of the second

$$-\varphi'' = k^2 \varphi, \qquad \varphi(0) = 0, \qquad \varphi(4) = 0, \tag{19}$$

which are even about $x = 2$. Expansion over the eigenfunctions of (19) is just a Fourier series problem.

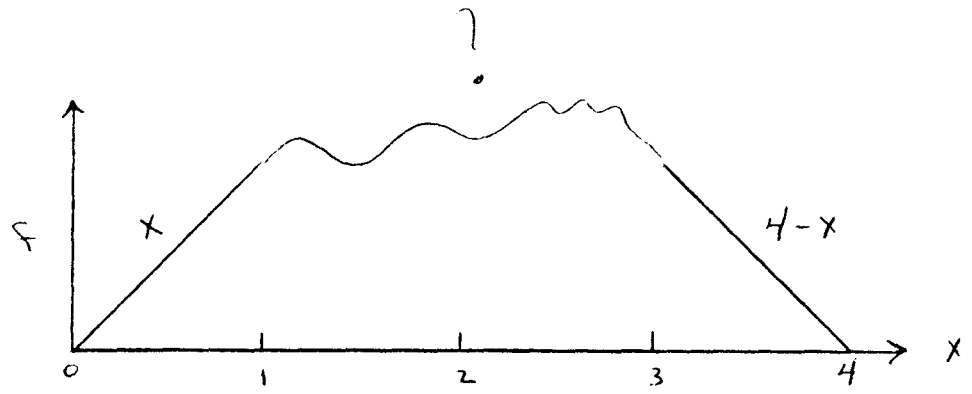
The values of the eigenfunctions of (19) between $0 \le x \le 1$ are just the same as that of the upper components of (13), $\varphi_n^{(1)}(x) = \sin k_n x$. So that the Fourier expansion of some given function over the solutions to (19) in the region $0 \le x \le 1$ will be just the same as the expansion $\sum_n \alpha_n \varphi_n^{(1)}(x)$. Now suppose we wish to expand

$$\begin{bmatrix} x \\ ? \end{bmatrix} \rightarrow \sum_n \alpha_n \Phi_n . \tag{20}$$

This will be the same as expanding

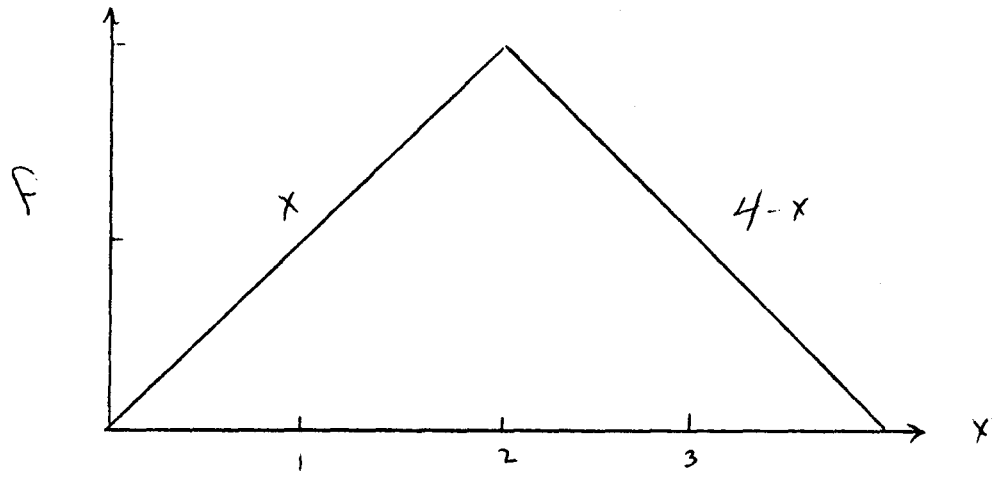
$$f(x) = \begin{cases} x & 0 \le x \le 1 \\ ?? & 1 < x < 3 \\ 4 - x & 3 \le x \le 4 \end{cases} \tag{21}$$

which is illustrated below



The idea is that we choose a function to connect from x = 1 to x = 3 so that the expansion converges as smoothly as possible between $0 \leq x \leq 1$.

A first, and it turns out satisfactory, choice on how to extend the function to be expanded from $x = 1 \rightarrow x = 2$ would be through analytic continuation. We just calculate the power series at x = 1 and extend it to x = 2. This is just matching the function and all of its derivatives at x = 1. In the above simple case this gives:



The expansion of this function converges uniformly at least for $0 \leq x \leq 1$. Hence we have obtained smooth convergence of $\sum_n \alpha_n \varphi_n^{(1)}(x)$.

Having chosen this power series technique, we proceed to evaluate the expansion coefficients:

$$\begin{aligned} \alpha_n &= \tfrac{1}{2} \int_0^4 f(x) \sin k_n x \\ &= \int_0^2 f(x) \sin k_n x \quad . \end{aligned} \tag{22}$$

We notice the following interesting, useful, but not accidental result

$$\sin k_n x = \cos k_n (2 - x). \tag{23}$$

So now

$$\alpha_n = \int_0^1 f(x) \sin k_n x + \int_1^2 f(x) \cos k_n (2 - x) \tag{24a}$$

$$= \int_0^1 f(x) \sin k_n x dx + \int_0^1 f(2 - y) \cos k_n y dy. \tag{24b}$$

The resemblence of Eq. (24b) to Eq. (17) suggests the following conclusion. Given $\begin{bmatrix} f(x) \\ ? \end{bmatrix}$ we take $f^{(2)}(x) = -f(2 - x)$, where a power series is used to calculate $f(y)$ for $1 \leq y \leq 2$.

When working on more complicated two-component eigenvalue systems, such as that of Siegert, equivalent eigenvalue problems may be difficult to find, and an interpretation and transposition of the lower component may be intractable. Some way of applying a power series method to calculate $f^{(2)}$ from $f^{(1)}$ is still needed. This is obtained by examining the application of the operator of the problem, L, to the vector to be expanded, that is, LF.

For the eigenvalue problem now under discussion [Eq. (14)], this is

$$LF = L\begin{bmatrix} f^{(1)}(x) \\ -f^{(1)}(2-x) \end{bmatrix} = \begin{bmatrix} f^{(1)\prime}(2-x) \\ -f^{(1)\prime}(x) \end{bmatrix} . \tag{25}$$

We see that LF necessarily satisfies the right-hand boundary condition, and in fact L^qF satisfies that condition for any q. The general rule to be adopted in the future is that given $f^{(1)}(x)$ then $f^{(2)}(x)$ will be chosen so that L^qF will satisfy the right-hand boundary condition for all q. This will completely specify $f^{(2)}$ by some kind of power series about x = 1 (or the right-hand boundary).

D. Next we consider problem C with a potential

$$-\varphi'' + U\varphi = k^2\varphi, \qquad \varphi(0) = 0 , \qquad \varphi'(1) = k\varphi(1) . \tag{26}$$

This gives the same form of the solutions, the same boundary conditions, and inner product. Finding the right form for the operator is a little tricky; the one chosen is

$$L\Phi_n = \begin{bmatrix} \varphi_n^{(2)\prime} \\ -\varphi_n^{(2)\prime} - \int_x^1 U(y)\varphi_n^{(2)}(y)\, dy \end{bmatrix} = k_n\Phi_n \tag{27}$$

The eigenvalue problem is no longer self-adjoint. The adjoint operator is given by

$$L^+\Phi_n^+ = \begin{bmatrix} \varphi_n^{+(2)\prime} - U(x)\int_0^x \varphi^{+(2)}(y)\, dy \\ -\varphi_n^{+(1)\prime} \end{bmatrix} = k_n\Phi_n^+ . \tag{28}$$

The eigenvalues for $U = U_0 = \text{const}$ are given by $k' \operatorname{ctn} k' = k$, $k' = \sqrt{k^2 - U_0}$. The eigenvectors are

$$\Phi_n = \begin{bmatrix} \sin k_n x \\ \dfrac{-k_n}{k'_n} \cos k'_n x + \left(\dfrac{k_n}{k'_n} - \dfrac{k'_n}{k_n} \right) \cos k'_n \end{bmatrix} \tag{29a}$$

$$\Phi_n^+ = \begin{bmatrix} \sin k_n x \\ \dfrac{-k'_n}{k_n} \cos k'_n x \end{bmatrix} \tag{29b}$$

The orthogonality condition is

$$\{\Phi_n^+, \Phi_\ell\} = N_n \delta_{n\ell} = \left[1 - \frac{\cos 2k'_n}{k_n}\right] \delta_{n\ell} .$$

The expansion formula, $F \rightarrow \sum_n \alpha_n \Phi_n$, works similarly to that of problem C, except that

$$\alpha_n = \frac{\{\Phi_n^+, F\}}{\{\Phi_n^+, \Phi_n\}} \tag{30}$$

The chosen condition for finding $f^{(2)}$ from $f^{(1)}$, namely, that $L^q F$ satisfy the right-hand boundary condition, produces good convergence. The lower component $f^{(2)}$ is still related to $f^{(1)}$ by a power-series-like relation, but it is no longer a simple reflection.

E. The Siegert problem was solved through the techniques developed in the study of the previous four problems. The principal difficulty was not finding expansion coefficients, but making the expansion converge.

The condition that $L^q F$ must satisfy the right-hand boundary condition was the crucial development.

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PROPOSITIONS

PROPOSITION I

Vibrational Excitation by Electron Impact-Raman Spectroscopy

It is proposed that vibrational excitation by electron impact be considered in the formalism of Raman spectroscopy. In specific, that one may thereby show that the 22 eV vibrational excitation structure observed in N_2 is mediated by the resonances associated with the grandparent $D\ ^2\Pi_g$ state of N_2^+.

There has been recent experimental interest in vibrational excitation of the ground electronic state of diatomic molecules by electron impact. In specific, it was found that the excitation amplitude shows broad maxima around 22 eV in N_2 (Ref. 1), 20 eV in CO (Ref. 2), and 8-15 eV in O_2 (Ref. 3). Pavolic et al. (Ref. 1) have proposed a heuristic explanation of the 22 eV structure in the N_2 cross section. Heuristic it has been indeed, in the dictionary sense,[4] to stimulate me to come up with an alternative.

The energy of the first vibrational transition of N_2 is only some 290 mV. As Pavlovic et al. rightly suggest, a strong enhancement near 22 eV (almost a hundred-fold energy excess) should be mediated by an unstable intermediate state--a resonance (i.e., one or more). But the statistical model of multiply excited resonances of Pavlovic et al. lacks the cutting edge necessary to make it convincing.

It is suggested herein that the 22 eV structure is probably due to only the intermediate N_2^- states found by attaching two Rydberg electrons to the $D\ ^2\Pi_g$ grandparent ion of N_2^+, and that the broadness of the structure

is due to the short life of the negative-ion state and to the steepness of its potential curve.

Sanche and Schulz [5] have discussed in detail how the various excited negative-ion resonances may be described as two Rydberg electrons attached to a positive-ion grandparent core, and that the lowest of resonances appears at 4.0 to 4.1 eV below the grandparent. To examine the possible N_2^+ grandparent ions we can look at the paper by Gilmore. [6] The likely candidates for 22 eV structure are the $C\ ^2\Sigma_u^+$ and $D\ ^2\Pi_g$, which are both about 25-26 eV above the ground state of N_2 in its Franck-Condon (F.-C.) region. I have empirically selected the $D\ ^2\Pi_g$ state as the victim since it alone is repulsive or on the repulsive wall in the Franck-Condon region.

There is another type of spectroscopy in which a particle impinges with far more energy than necessary for the transition of interest. One then looks at the energy loss spectrum. That would be Raman spectroscopy. The theory of Raman spectroscopy, as discussed by Ting, [7] relies on a virtual transition to an intermediate state. Ignoring the angular dependence, the matrix element reads something like

$$T_{fi} = \sum_n M_{on} M_{no} \{ \sum_k \langle of|nk\rangle \langle nk|oi\rangle \cdot [\frac{1}{(\epsilon_{nk} - \epsilon_{of} - E)} + \frac{1}{(\epsilon_{nk} - \epsilon_{oi} + E)}]. \quad (1)$$

The letter n labels the intermediate rotational-electronic state, the letter o the initial and final rotational-electronic states. The letters k, i, and f similarly label the vibrational subcomponents of these states. The dipole transition operator has disappeared into the electronic matrix elements. The $\langle\ |nk\rangle$ are just Franck-Condon factors. Following Albrecht [8] for the

resonance-Raman effect, introducing $\Delta_{fk} = \epsilon_{of} - \epsilon_{nk}$ and $\Delta_{ki} = \epsilon_{nk} - \epsilon_{oi}$, the damping term $i\gamma$, and restricting the summation (1) to only one intermediate electronic state, we have

$$T_{fi} = M_{on}M_{no}\sum_k \langle of|nk\rangle\langle nk|oi\rangle \cdot \left[\frac{1}{\Delta_{fk} - E + i\gamma} + \frac{1}{E - \Delta_{ki} + i\gamma}\right]. \quad (2)$$

Now we suppose that $E \approx \Delta_{ki}$ and keep only the second term. Since the intermediate state $|nk\rangle$ is a vibrational continuum we need to evaluate

$$T_{fi} = M_{on}M_{no}\int d(\Delta_{ki})\frac{\langle of|nk\rangle\langle nk|oi\rangle}{(E - \Delta_{ki} + i\gamma)} . \quad (3)$$

To evaluate the integral (3) we first examine the Franck-Condon delta function reflection principle[9] for continuous initial or final states. Let B be the excitation energy of the $D\ ^2\Pi_g$ (N_2^+) state above the $X\ ^1\Sigma_g^+$ (N_2) state at the equilibrium distance (Re) of the latter, and let A be the slope of the $D\ ^2\Pi_g$ (N_2^+) curve at that point. Then we may evaluate

$$\begin{aligned}\langle nk|oi\rangle &= \int_0^\infty \delta[\Delta_{ki} + A(R - Re) - B]\psi_{oi}(R)dR \\ &= \psi_{oi}[Re + (B - \Delta_{ki})/A]/A\end{aligned} \quad (4)$$

and similarly for $\langle of|nk\rangle$. Finally if we set $\eta = [B - \Delta_{ki}]/A$, then

$$T_{fi} = Q\int \frac{\psi_{of}[Re + \eta]\psi_{oi}[Re + \eta]d\eta}{(E - B + i\gamma)/A + \eta} , \quad (5)$$

where Q is a constant without vibrational dependence.

Even replacing the vibrational wavefunctions by harmonic oscillator solutions leaves the integral (5) still too difficult to work out analytically.

But the general form may be imagined. When E - B is small, then the denominator will be smallest for $\eta \simeq 0$, i.e., the center of the F.-C. region, the numerator is generally the largest in that region as well. So it should be expected that $T_{fi}(E)$ have its maximum near the vertical excitation energy, B. We may evaluate the maximum value of $T_{fi}(E)$ as follows.

Set E - B to zero; then

$$T_{fi}(\max) = Q \int \frac{\varphi_f(\eta)\, \varphi_i(\eta) d\eta}{i\gamma/A + \eta} \quad . \tag{6}$$

Since the principal portion of the integral is to come from the vicinity of $\eta = 0$, we try the asymptotic expansion

$$T_{fi}(\max) = \frac{Q}{i\gamma/A} \int_{-\infty}^{\infty} \varphi_f(\eta)\varphi_i(\eta) d\eta \sum_n [-\eta/(i\gamma/A)]^n \tag{7}$$

and keep the first term that survives. This gives

$$T_{f0}(\max) = \frac{Q(-1)^f}{(i\gamma/A)^{f+1}} \frac{\sqrt{f!}}{(2\alpha)^{f/2}} \quad , \tag{8}$$

where α is the scaling constant of the oscillator $\alpha = m\omega/\hbar$. Finally,

$$|T_{f0}(\max)|^2 = Q^2 (A/\gamma)^{2(f+1)} \frac{f!}{(2\alpha)^f} \quad . \tag{9}$$

At this point it is time to compare with experiment.

First we consider the position of the maximum. Pavlovic et al. find the maximum in all three channels $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$ of N_2 to be around 22 eV. According to the empirical rule of Sanche and Schultz,

which says that the first (i.e., $3s\sigma$) resonance is 4.1 eV below the grandparent. The $D\ ^2\Pi_g\ (N_2^+)$ based resonance should have about 25.5-4.1 = 21.4 eV as its vertical excitation energy. Some contribution of the $3p\sigma$ resonance that should occur at 25.5 - 3.4 = 22.1 eV could also be present. In any case, the present theory is in complete accord with the experiment concerning the peak position.

A second test of the theory is available from the relative intensities of the $0 \rightarrow 1$, $0 \rightarrow 2$, $0 \rightarrow 3$ transitions. Equation (9) gives

$$|T_{20}/T_{10}|^2 = \frac{(A/\gamma)^2 2}{(2\alpha)} = (1/\alpha)(A/\gamma)^2 \qquad (10a)$$

$$|T_{30}/T_{20}|^2 = (A/\gamma)^2(6/2)(1/2\alpha) = (3/2\alpha)(A/\gamma)^2 \qquad (10b)$$

so

$$\frac{|T_{30}|^2|T_{10}|^2}{|T_{20}|^4} = 3/2 \ . \qquad (11)$$

Examination of the experimental results of Pavlovic et al. gives $|T_{10}|^2 = 12.5 \times 10^{-19}$, $|T_{20}|^2 = 2.75 \times 10^{-19}$, and $|T_{30}|^2 = 1.05 \times 10^{-19}$. Evaluation of the ratio as in Eq. (11) gives 1.74, which is easily within the experimental error (signal-to-noise 3-1, see Ref. 1) of the predicted value of 1.5.

Finally we look at the dependence on E. Suppose E - B in Eq. (5) is large. The principal portion of the integral will still come from the F.-C. region, $\eta \simeq 0$. So we expand

$$T_{fi}(E) \approx Q/[(E - B)/A] \int \varphi_f(\eta)\varphi_i(\eta)d\eta \sum_n \left[\frac{-\eta}{(E - B)/A}\right]^n . \qquad (12)$$

This gives

$$T_{fo}(E) \simeq \frac{Q(-1)^f \sqrt{f!}}{[(E-B)/A]^{f+1}(2\alpha)^{f/2}} \tag{13a}$$

or

$$|T_{fo}(E)|^2 \sim \frac{1}{|E-B|^{2(f+1)}} \tag{13b}$$

$$|T_{10}(E)|^2 \sim \frac{1}{(E-B)^4} \tag{13c}$$

$$|T_{20}(E)|^2 \sim \frac{1}{(E-B)^6} \tag{13d}$$

$$|T_{30}(E)|^2 \sim \frac{1}{(E-B)^8} \tag{13e}$$

Comparison with the curves of Pavlovic et al. shows indeed that the tails seem to get sharper as f increases.

The change over from E - B small to E - B large will depend in general on the size of the F.-C. region (i.e., α), the energy spread (i.e., the slope of the upper curve A), and the decay width (γ). Indeed the validity of Eqs. (9) and (13) depends on these same factors.

It is proposed that the single grandparent state, D $^2\Pi_g(N_2^+)$, provides the explanation of the 22 eV structure observed in the vibrational excitation spectrum observed by Pavlovic et al. The formalism of Raman spectroscopy will provide an avenue for the numerical description of the process. A specific observation of importance is that the intermediate state is either repulsive or on the repulsive wall in the

Franck-Condon region of the ground state. A similar procedure should work for vibrational excitation in other molecules, in specific, CO and O_2.

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PROPOSITION II

The Princess and the Monster

It is proposed that the optimum strategies for pursuit games with no information may be found merely by using the fact that capture has not yet occurred.

The princess and the monster[1] are locked in a dark room. The monster searches for the princess, moving with simple motion (arbitrary curvature) at a known speed. The princess seeks to avoid capture, with complete freedom of locomotion. How should the monster proceed? How long can the princess avoid capture?

Such is a pursuit game with no information. Herein is presented the solution to the similar but much simpler problem in which the antagonists are confined to a simple closed curve. This game is simple enough to be solvable by more classical game-theoretic techniques,[2] but is here solved through the proposed procedure of gaining information from the fact that the game has not yet finished. The solution of the original game above, to be played in a room of arbitrary shape awaits the fuller development of the ideas presented.

We begin the discrete version of this game. The players each occupy one of n (≥ 3) points on the circumference of a circle with equiprobable relative distribution. They move simultaneously, the monster transferring his position to either of the adjacent points, the princess standing still or taking one or more steps either to the left or right. Capture occurs when both players occupy the same point or attempt to pass through each other. The payoff to the monster is the chance of catching the princess in the present turn. Alternately, the game

continues until capture with the payoff to the princess being the number of turns she lasted.

The first turn is easy to work out. The monster has two pure strategies available: to move left (L) or to more right (R). The princess has several: to remain stationary (S), one step left or right (L or R), on k steps left or right (k · L or k · R). This is represented in the game matrix[3, 4]

M \ P	S	L	R	k · L	k · R
L	$\frac{1}{(n-1)}$	0	$\frac{2}{(n-1)}$	$\frac{k-1}{(n-1)}$	$\frac{k+1}{(n-1)}$
R	$\frac{1}{(n-1)}$	$\frac{2}{(n-1)}$	0	$\frac{k+1}{(n-1)}$	$\frac{k-1}{(n-1)}$

The entires are the payoffs, i.e., the chance of capture if the princess and monster adopt the strategies indicated. For example, if the princess is stationary, the monster searches one of her n - 1 possible starting positions by moving either L or R.

Let us first examine the possibility of the princess moving more than one step, say k · L. Examination of the payoffs above shows that for $k > 1$ the princess is always more likely to be captured regardless of what the monster does than if she had chosen just L. Hence her optimum strategy is to move no faster than the monster.

Next we see that the monster can have no preference between L and R. To keep the princess confused he flips a coin: 50% L + 50% R.

This means also that the princess has no directional preference. We rewrite the matrix including all this

M \ P	S	L or R
L or R	$\frac{1}{(n-1)}$	$\frac{1}{(n-1)}$

The optimum strategies for the first turn are

$$\text{monster} = \tfrac{1}{2}L + \tfrac{1}{2}R$$

$$\text{princess} = P \cdot S + (1 - P) \cdot (\tfrac{1}{2}L + \tfrac{1}{2}R) .$$

Any mixture of movement and inertia is acceptable to the princess. The value of the game (chance of capture) is $1/(n - 1)$. We now specify without loss of generality that the princess and monster will each take one step each turn.

The second turn is a great deal more complicated. Determination of the optimum strategies requires a complete description of the principle that is proposed. The strategies are specified by two parameters for each player, α_M and α_R, which give the probability of changing or repeating the direction, respectively. The only pieces of information available to the two opponents are the knowledge of their own previous movements and the fact that capture has not yet occurred.

The criterion of an optimum strategy is basically as follows. When the monster uses his optimum strategy, even if the princess knows that strategy (that means the probabilities) there is nothing she can do to improve her position.[5] Whatever she does will produce a

payoff the same as or worse than the value of the game. Finding the optimum strategy will mean having each player adjust his strategy (choose his parameters α_M and α_R) so that it does not matter what his opponent does.

In specific, we presume that the princess knows the monster's best strategy, and knows that he is following it. If the monster followed his 50/50 best strategy in turn one, then (presuming she was not captured), the princess can estimate the chance of his having gone in the same or opposite direction as she did. This results in the "weight" matrix

M \ P	L	R
L	$\frac{1}{2}\frac{(n-1)}{(n-2)}$	$\frac{1}{2}\frac{(n-3)}{(n-2)}$
R	$\frac{1}{2}\frac{(n-3)}{(n-2)}$	$\frac{1}{2}\frac{(n-1)}{(n-2)}$

which was obtained by taking the monster's 50/50 strategy, reducing the likelihood of their moving in opposite directions due to the chance of capture, and normalizing the columns to unity.

Now we must calculate the capture amplitude matrix for the second turn. This is just a cross-listing of the probability of capture on the second turn presuming that the princess was not captured in turn one.

M \ P	LL	LR	RL	RR
LL	0	$\frac{2}{(n-1)}$	0	$\frac{2}{(n-3)}$
LR	$\frac{2}{(n-1)}$	0	0	0
RL	0	0	0	$\frac{2}{(n-1)}$
RR	$\frac{2}{(n-3)}$	0	$\frac{2}{(n-1)}$	0

Now suppose the princess went L in turn one. The chance that the monster also went L is $\frac{1}{2}\frac{(n-1)}{(n-2)}$. If she goes L again, the only way he can catch her is by going R. The chance of catching her in this case is $\frac{2}{(n-1)}$. The monster has a probability of α_M of changing direction after turn one. So the total payoff or capture amplitude is

$$\frac{1}{2}\frac{(n-1)}{(n-2)} \cdot \frac{2}{(n-1)} \cdot \alpha_M = \frac{\alpha_M}{(n-2)} .$$

Similarly, princess LL vs monster R? gives

$$\frac{1}{2}\frac{(n-3)}{(n-2)} \cdot \frac{2}{(n-3)} \alpha_R = \frac{\alpha_R}{(n-2)}$$

Princess LR vs monster L? gives

$$\frac{1}{2}\frac{(n-1)}{(n-2)} \frac{2}{(n-1)} \alpha_R = \frac{\alpha_R}{(n-2)} .$$

Finally, princess LR vs R? gives zero since there would be no way

for the monster to get her.

All of this is summarized in the following matrix

M \ P	L	R
	$\frac{(\alpha_M + \alpha_R)}{(n-2)}$	$\frac{\alpha_R}{(n-2)}$

By the min-max principle the monster wishes to choose his parameters to make the payoffs equal for the princess. Hence he chooses $\alpha_R = 1$, $\alpha_M = 0$. That is, the monster always takes two steps in the same direction. By continuing this process into the third and subsequent turns we find that the monster continues to travel toward the other side of the circle--until he gets there.

When enough time has elapsed for the monster to get to the opposite side of the circle, the princess can figure out which direction he is going (a plus for her). Continuing the game to the next move, we find that the best strategy for the monster is to confuse the princess. He pretends that this is now the first turn. He flips a coin to choose the direction and rushes to the opposite side of the circle again. Each time the monster goes to the opposite side he has a one-half chance of catching the princess.

The point of this long-winded discussion was to illustrate specifically how information can be gained from the lack of capture. It is expected that this idea will be instrumental in the solution of more complicated games of pursuit. A plausible solution to the original

princess and the monster problem is that the monster randomly chooses a way to search half (or at least some fraction) of the room, and when he is done with that search he randomly guesses again.

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2. To the best of my knowledge, no solution has been published.
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5. This is von Neumann's min-max principle; see Refs. 3 and 4 for details.

PROPOSITION III

The Schwinger Variational Principle

It is proposed that certain simplifications including finite-basis-set-expansion and a suitable and convenient approximation of the necessary Green's function will permit the efficient use of the Schwinger variational method for describing electron-atom and electron-molecule scattering.

The Schwinger variational principle has been around for some time[1] but its expected application to electron-atom and electron-molecule scattering has failed to materialize. This result is probably due to the apparent complexity of the method. It is against this complexity that an effort is to be made.

We first examine the Schwinger variational method and the solution to the variational equations in some detail. The Schwinger form is

$$T_{ba} = \frac{\langle \Psi_b^{(-)}, V\varphi_a \rangle \langle \varphi_b, V\Psi_a^{(+)} \rangle}{\langle \Psi_b^{(-)}, (V - VGV)\Psi_a^{(+)} \rangle} , \qquad (1)$$

where φ_a is the initial given plane-wave state

φ_b is the final given plane-wave state

$\Psi_b^{(-)}$ is the outgoing wave corresponding to φ_b

$\Psi_a^{(+)}$ is the incoming wave corresponding to φ_a

V is the scattering potential

G is the resolvent, "Green's Function," or propagator[2] for the zero-order Hamiltonian.

T_{ba} is the transition matrix element between initial state φ_a and final state φ_b.

To illustrate the variational nature of the method, and to find the optimum $\Psi_a^{(+)}$, we examine the variation of T_{ba}, δT_{ba} due to $\delta\Psi_b^{(-)}$.

$$\delta T_{ba} = \frac{\langle \delta\Psi_b^{(-)}, V\varphi_a\rangle\langle V\varphi_b, \Psi_a^{(+)}\rangle}{\langle \Psi_b^{(-)}, (V - VGV)\Psi_a^{(+)}\rangle} - T_{ba}\frac{\langle \delta\Psi_b^{(-)}, (V-VGV)\Psi_a^{(+)}\rangle}{\langle \Psi_b^{(-)}, (V - VGV)\Psi_a^{(+)}\rangle} \tag{2}$$

Setting $\delta T_{ba} = 0$ gives

$$\langle \delta\Psi_b^{(-)}, [V\varphi_a\rangle\langle \varphi_b, V\Psi_a^{(+)}\rangle - T_{ba}(V - VGV)\Psi_a^{(+)}\rangle] = 0 \ . \tag{3}$$

If $\delta T_{ba} = 0$ for any $\delta\Psi_b^{(-)}$, then

$$[|V\varphi_a\rangle\langle V\varphi_b| - T_{ba}(V - VGV)]\Psi_a^{(+)} = 0 \ . \tag{4}$$

We divide $\Psi_a^{(+)}$ into two parts, one parallel to $V\varphi_b$ and one perpendicular to $V\varphi_b$,

$$\Psi_a^{(+)} = \beta[V\varphi_b + q] \ , \qquad \langle q, V\varphi_b\rangle = 0 \ , \tag{5}$$

where β is an arbitrary constant to make the normalization come out right. Then

$$|V\varphi_a\rangle\langle V\varphi_b, V\varphi_b\rangle\beta - T_{ba}(V - VGV)\Psi_a^{(+)} = 0 \tag{6a}$$

or

$$(V - VGV)\Psi_a^{(+)} = [\frac{\langle V\varphi_b, V\varphi_b\rangle}{T_{ba}}\beta]\, V\varphi_a \ . \tag{6b}$$

Now we assume V is invertible, set $\beta = T_{ba}/\langle V\varphi_b, V\varphi_b\rangle$, and get

$$\Psi_a^{(+)} = \varphi_a + GV\Psi_a^{(+)} \quad , \tag{7}$$

which is the integral equation for scattering, exactly equivalent to Schrödinger's equation.

The Schwinger method has several advantages that make it attractive.

1. The Schwinger form above is homogeneous of order zero in the trial functions. Hence this method is independent of normalization, unlike the Kohn and Hulthén methods.[3]
2. There is no need to worry about the boundary conditions since the presence of the potential V in each integral emphasizes the region of interaction, which is what we are really interested in anyway. The Kohn and Hulthén methods are based on precisely these boundary conditions.[3]
3. The method is direct and unambiguous. There are no choices of conditions, spurious singularities (as in the Kohn method[3]) or ad hoc assumptions (as in the Harris method[3]).
4. Finally, the Schwinger method allows the application of the same consistent formalism to elastic, resonance, and inelastic scattering.

For electron-atom and electron-molecule scattering, the principal difficulty revolves about the difficulty of the VGV integral--the integral needed for the seldom-used Second-Born approximation.[4, 5] That is,

1. We need to evaluate complicated integrals involving Green's functions.

2. For systems more complicated that $e^- - H$, we do not even know the Green's functions.

Several suggestions are to be made that should help to remove these problems. These suggestions will be illustrated in the context of electron-hydrogen atom scattering. The total Hamiltonian (in atomic units) is

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 + 1/r_{12} . \tag{8}$$

We set $h_1 = -\tfrac{1}{2}\nabla_1^2 - 1/r_1$, $h_2 = -\tfrac{1}{2}\nabla_2^2$, and $V = -1/r_2 + 1/r_{12}$. The zero-order Hamiltonian is to be

$$H_0 = h_1 + h_2 . \tag{9}$$

We need to construct the Green's function for H_0 called $G_0(E)$. Following Davydov[6] $G_0(E)$ can be written as

$$G_0(E) = \sum_n G_2(E - \epsilon_n) |\Psi_n\rangle\langle\Psi_n| , \tag{10}$$

where G_2 is the Green's function for h_2 and Ψ_n's are the eigenstates of h_1 with energies ϵ_n. Equivalently,

$$G_0(E) = \int \frac{d^3k}{(2\pi)^3} G_1(E - k^2/2) |\varphi_{\hat{k}}\rangle\langle\varphi_{\hat{k}}| , \tag{11}$$

where $\varphi_{\hat{k}} = e^{i\hat{k}\cdot\hat{r}}$ and G_1 is the Green's function for h_1.

Now we are to find an approximation to G_1. Ignoring for the moment permutational symmetry and spin, and choosing a finite set of one-electron basis functions $\{\eta_i\}$, we intend to diagonalize h_1 in this basis and try to construct an approximate Green's function. The only question is what eigenvalue to assign to vectors outside the finite basis

$\{\eta_i\}$. Suppose we select the number α. This defines a new Hamiltonian,

$$h_1^{\alpha} = P h_1 P + \alpha(1 - P) , \tag{12}$$

where $P = \sum_i |\eta_i\rangle\langle\eta_i|$ is the projection onto the finite basis. Now let $\{\xi_k\}$ and $\{\bar{\epsilon}_k\}$ be the eigenfunctions and eigenvalues of $\bar{h}_1$ in the basis $\{\eta_j\}$. The exact Green's function for h_1^{α} is then

$$G_1^{\alpha}(E) = \frac{(1 - P)}{\alpha - E + i\delta} + \sum_j \frac{|\xi_j\rangle\langle\xi_j|}{\bar{\epsilon}_j - E + i\delta} \tag{13}$$

where δ is to go to zero in the usual sense.[6] A considerable simplification will result if we let α be very large. This gives

$$G_1^{\infty} = \sum_j \frac{|\xi_j\rangle\langle\xi_j|}{\bar{\epsilon}_j - E + i\delta} . \tag{14}$$

The Green's function for h_1, $G_1(E)$ has a sequence of poles, at $E = \epsilon_j < 0$, and a branch line, $E = k^2/2m > 0$. $G_1^{\infty}(E)$ has a similar set of poles, $E = \bar{\epsilon}_j$; but no branch line. If E is close to one of the poles of $G_1(E)$, say $E = \epsilon_k$, then we expect the behavior to be dominated by that pole, or at least the closest two or three. If G_1^{∞} has nearly the same poles as $G_1(E)$ near ϵ_k and nearly the same residue at each as $G_1(E)$, then $G_1^{\infty}(E)$ should be a very good approximation to $G_1(E)$ in the vicinity of ϵ_k. The contribution from the other poles and the branch line should be smoothly approximated by the other poles of $G_1^{\infty}(E)$ not necessarily close to those of $G_1(E)$, and with residues not necessarily close to those of $G_1(E)$. The approximation will improve as more basis functions (η_i's) are added. It is very important to note that all of the eigenvalues $\{\bar{\epsilon}_i\}$

are to be included, even those that are very poor approximations to the bound states of h_1. Only in this way can the continuum contributions to G_1 be approximated.

Now consider expanding $\Psi_a^{(+)}$ and $\Psi_b^{(-)}$ in terms of the two-electron basis $\{\eta_i\eta_j\}_{i,j}$. This corresponds to the insertion of projection operators in the Schwinger form as

$$\bar{T}_{ba} = \frac{\langle P\Psi_b^{(-)}, V\varphi_a\rangle\langle V\varphi_b, P\Psi_a^{(+)}\rangle}{\langle P\Psi_b^{(-)}, (V - VGV)P\Psi_a^{(+)}\rangle} \quad . \tag{15}$$

Variation yields

$$\begin{aligned} \bar{\Psi}_a^{(+)} &= [P(V - VGV)P]^{-1}PV\varphi_a \\ T_{ba} &= \langle V\varphi_b, P[P(V - VGV)P]^{-1}PV\varphi_a\rangle \quad . \end{aligned} \tag{16}$$

The only complicated part will come in expressing P(V - VGV)P. To do that we note that we only need integrals of the form $\langle \eta_i\eta_j | V | \eta_k\eta_\ell\rangle$ and $\langle \eta_i\eta_j | VG_0(E)V | \eta_k\eta_\ell\rangle$. These are first- and second-Born integrals. The whole point in the approximation of the Green's function for h_1 above is that now

$$\langle \eta_i\eta_j | VG_0^{\infty}(E)V | \eta_k\eta_\ell\rangle = \sum_m \langle \eta_i\eta_j | VG_2(E - \bar{\epsilon}_m) | \xi_m\rangle\langle \xi_m | V | \eta_k\eta_\ell\rangle, \tag{17}$$

since the ξ_m's are linear combinations of the η_i's. This expression reduces to just a sum of one-electron-like second-Born integrals that are definitely tractable. All of the complexity of the bound-part Green's function has disappeared.

Further, it turns out that by making the replacement of G_1 by G_1^∞ and h_1 by h_1^∞, the scattering problem expressed in this basis, with the zero-order Hamiltonian $h_1^\infty + h_2$ has been solved exactly. But, since the scattering perturbation would not be $V + h_1^\infty - h_1$, we might expect spurious scattering due to $h_1^\infty - h_1$. One can show that no troubles will occur. The inclusion of permutational, spin, and spatial symmetries merely becomes a symmetrization of the matrix $\langle \eta_i \eta_j | V\text{-}VGV | \eta_k \eta_\ell \rangle$ after construction and before inversion.

It is to be noticed in passing that if the two-electron basis $\{\eta_j \varphi_{\hat{k}}\}$, where the η_j's are some of the exact H-atom bound states and the $\varphi_{\hat{k}}$'s are plane waves, is chosen, the Schwinger principle and use of the above Green's function produces the close-coupling method as a special case.

It is proposed that the expression of the Schwinger variational principle over a finite, conveniently chosen basis-set, a special choice of the zero-order Hamiltonian so that it has a simple and convenient Green's function, and the final application of the symmetries of the problem will allow consistent and convenient application of the principle to electron-atom and electron-molecule scattering. The Schwinger method should become at least as efficient as the close-coupling method.

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PROPOSITION IV

Charge Extrapolation, Resonances, and Local Potentials

It is proposed that a study of atomic states and configurations as functions of nuclear charge will provide

1) approximation wavefunctions and energies of and a characterization of shape resonances of the type (1s)(ns), (1s)(np) of H^- and $(1s)^2(ns)$, $(1s)^2(np)$ of He^-, etc., and
2) local potentials for unbound states for use in scattering or molecular-bound-state calculations.

The wavefunction for an electron moving near a hydrogen atom is conveniently thought of as resembling the diffuse orbital of H^-. The vicinity of a helium atom is more difficult to describe. No bound states of He^- exist so there are no orbitals as fixtures for the imagination. One might hope nonetheless to be able to find a simple expression of the attractive and repulsive forces seen by an electron near the He atom.

In the case of H^- those same forces can be easily and fairly accurately represented by a local potential.[1] This local potential can be obtained by solving the equation (in a.u.)

$$[\tfrac{1}{2}\nabla^2 + V]\varphi_2 = \epsilon_2 \varphi_2 \quad \text{or} \quad V = \epsilon_2 + 1/2\varphi_2 \, \nabla^2 \varphi_2 \qquad (1)$$

for V, given φ_2 and ϵ_2 from a G1 calculation. According to the current formalism, this potential should only be used for the s-wave portion of an orbital since it came from an s-orbital in the first place.[2] To find this local potential we must first solve for the lowest bound state.

This is possible for ^1S Li^-, but for most of the other simple ionic states it fails, e.g., ^3S, ^1P H^-, ^2S, ^2P He^-, ^1P Li^-. Now we ask, is there a state of ^2S He^- from which a local potential can be obtained? There is no such bound state, but there may be an almost bound state--a resonance.

A resonance state is really very close to what is needed. It is understood to be concentrated near the atom. For a short distance out from the nucleus the wavefunction should look just as He^- would be expected to look, say, like the configuration (1s)(1s′)(2s). Asymptotically, it is a plane wave, being an unbound state. Although the outer orbital from this state, concentrated mostly near the atom, would seem to be a good candidate, it is unavailable. The normal SCF methods do not work for unbound states or resonances. We will instead try to approximate this state and the local potential by extrapolation from the isoelectronic series with the same configuration.

As an indication of the plausibility of this procedure we will try to measure the smoothness with which the orbitals change from one nuclear charge to the other. This is done by making graphs of the ionization potentials of the various species. Naturally, the ionization potential of the outer electron in the series Li, Be^+, B^{+2}, C^{+3}, etc., will become larger due to the increased charge of the nucleus. More useful would be a measure of the changing effect of the inner electrons. An estimate of the ionization potential of Li would be $\frac{1}{2 \cdot 2^2}(3-2)^2 =$ 0.125 a.u. or $\frac{1}{2n^2}(Z - Z_{core})^2$, where n is the principal quantum number of the outer orbital and Z_{core} is the number of underlying electrons. So we plot $\Delta(Z) = IP(Z) - (1/2n^2)(Z - Z_{core})^2$. As an example, a plot of

$\Delta(Z)$ for the $(1s)(1s')(ns)$ series is shown in Fig. 1.

For this and the similar 2, 3, and 4 electron isoelectronic series, the points are incredibly close to being collinear. Apparently what changes from one charge to the other does so very smoothly. The limiting values, found by parabolic fit to the last three points, are shown in Table I. We note that $IP(Z_{core}) = \Delta(Z_{core}) < 0$ implies instability. As expected, the lowest ^1S states of H^- and Li^- are predicted to be stable. Far more remarkable is the appearance of the $(1s)(1s')(2s)\ ^2S$ resonance of He^- near 0.5 eV. These extrapolations further predict that no others will be found in e^--He or e^--Li scattering. We see from Table I that the lower s-wave resonances should be too close together and too close to zero to be separable or detectable. The p-wave resonances will be very hard to detect since $\sigma_1 \sim k^2 \sim E$ for small momentum k or energy E. The expected resonance cross section should be swamped by the factor of k^2 since the resonance energy is so small. These successes in extrapolation build our confidence in the idea.

It is remarkable that the curves and the predicted energies of the resonances are all out of order. The least stable is the 2p, then the 3p, then the 4p, and so on. The configurations crossed each other and inverted their order. This is at first surprising but becomes less so after some thought. A 2p resonance would be one that has an outer orbital with no radial nodes near the nucleus and is generally the same shape as a bound 2p orbital. A 3p resonance should have one radial node and be more diffuse than a 2p. We would say that the 2p should

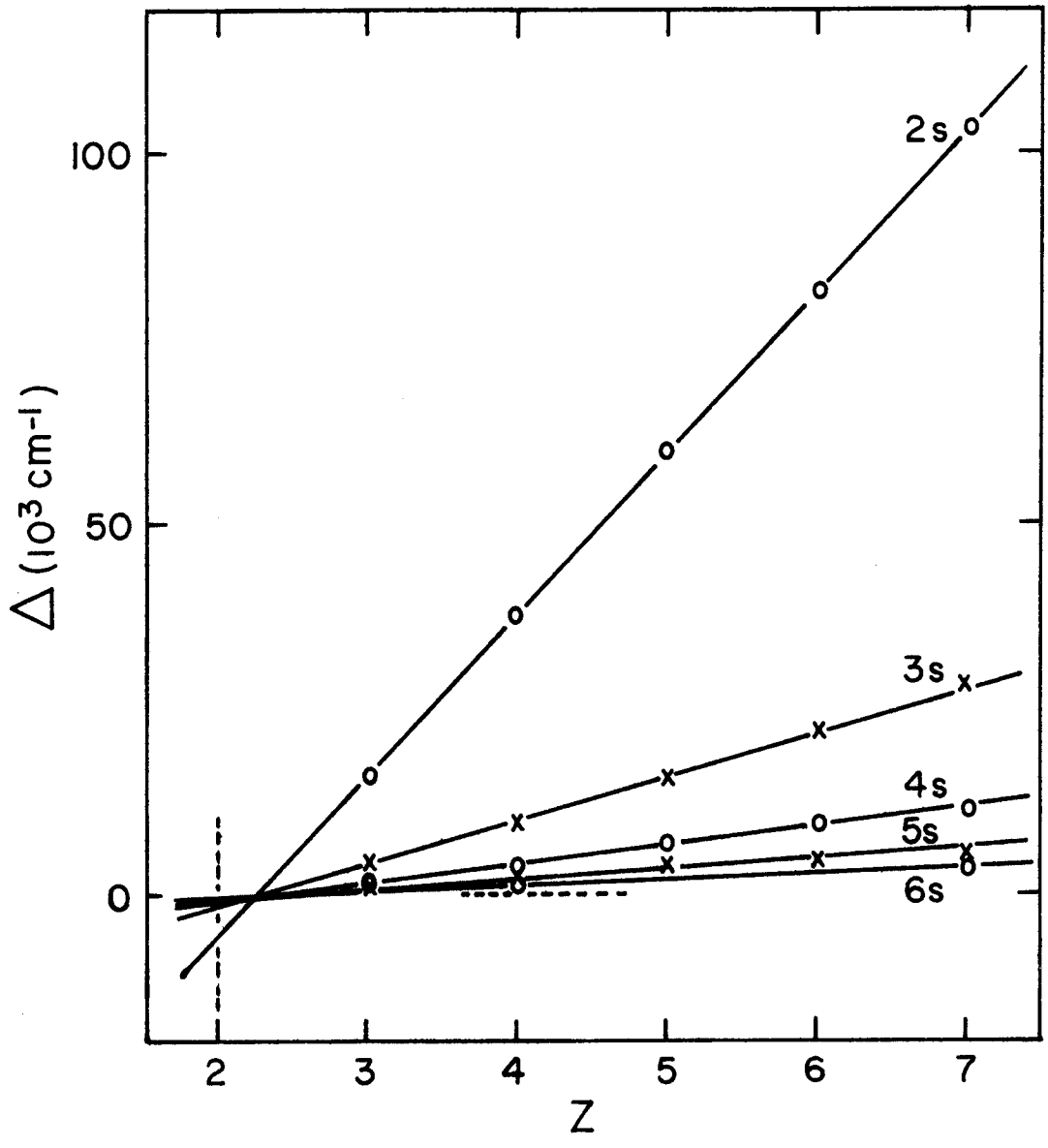

Fig. 1. $He^- {}^2S_{\frac{1}{2}}$ (1s)(1s′)(ns) series, extrapolation of the correction to the ionization potential. Data taken from Refs. 3-5.

TABLE I. Predicted resonance energies from isoelectronic charge extrapolation.[a]

Ion	State	E = -I.P.		
		cm^{-1}	eV	a.u.
H^-	$1s\ ^1S$	-6100	-0.755	-0.0278
	$2s\ ^3S$	+2400	+0.30	+0.011
He^-	$2s\ ^2S$	4252	0.53	0.019
	3s	1378	0.17	0.0063
	4s	588	0.073	0.0028
	5s	53	0.006	0.0002
	$2p\ ^2P$	1550	0.19	0.0071
	3p	493	0.061	0.0023
	4p	214	0.026	0.0010
	5p	108	0.013	0.0005
Li^-	$2s\ ^1S$	-3049	-0.378	-0.014
	3s	+ 525	+0.065	+0.0024
	$2p\ ^1P$	6809	0.85	0.031
	3p	4144	0.51	0.019

[a] Data taken from Refs. 3-5.

have a lower energy since it has fewer nodes. This logic no longer applies because far from the nucleus both the 2p and 3p resonance orbitals behave as plane waves, the real part of which has infinitely many nodes. No comparison on the basis of nodes is possible. The 2p is expected to be tighter than the 3p. It appears that the potentials they see are mostly repulsive at short range (no bound state exists). The 2p being tighter could be concentrated in a region of higher repulsive potential than the 3p; hence it would have a higher energy.

A comment should now be made on the observations of Gerjuoy[6] and Kaplan and Kleiner.[7] These observations showed that if $He^{-}\ ^2P$ is unstable then $Z^{Z-3}\ ^2P$ is stable for any $Z > 2$. We can see that this is true for say $Z = 2 + \epsilon$, $\epsilon > 0$. For sufficiently large r the potential seen by the outer electron will be just $-\epsilon/r$. This is enough to bind the electron no matter how small ϵ is. But as ϵ becomes smaller and smaller, the np configurations cross each other. The most stable state should nearly follow the most stable configuration at each ϵ. The character of the lowest state just changes from 2p to 3p to 4p to ... to ∞p as $\epsilon \rightarrow 0$.

We have seen that the ionization potential extrapolates very smoothly and should give good resonance energies. It is claimed that the outer orbital of approximate wavefunctions for these states will extrapolate just as smoothly. It is proposed that we obtain approximate resonance wavefunctions by just this extrapolation of the orbitals. We would like a local potential to describe the region near the atom. It is proposed that we take the orbitals describing the lowest, tightest bound

state--which extrapolates to the highest, tightest resonance--then construct the local potentials for the bound states and extrapolate to get the local potential for the resonance.

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PROPOSITION V

A Valence Bond View of Solids[1]

The idea of viewing conduction in solids as resonating valence bond structures has been around for some time. But it has been in disrepute due to the calculational successes of band theory. It is proposed that the ability to think in chemical terms will make the valence bond view worth the effort.

Over the years the Hartree-Fock approximation and group theory have made enormous strides in the understanding of the electronic structure of periodic solids. Implicitly the electronic structure becomes a bulk property of the periodic lattice; the individual orbitals are then completely delocalized Block states.[2] Theoretically, the study of solids would consist mostly in finding the effective potential that the conducting electrons see and computing the band structure therefrom.

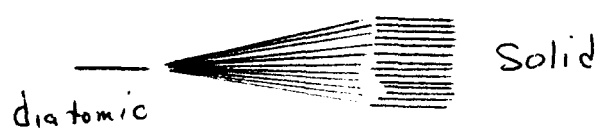
There are a number of reasons to think that the present band-theoretic techniques are near their apex, and that one might look next in other directions. To me the most important of these reasons is chemistry. A solid is just an immense molecule. The atoms do not just set up an effective potential, they form bonds to each other. Valence should dominate. The second reason is symmetry. The band theory depends crucially on the fact that the solid is periodic. The predicted structure changes drastically when the symmetry is reduced (e.g., in doped or amorphous solids). Intuitively and experimentally we know that a small amount of impurity usually produces a small effect.

The conclusion then is to look for an alternate description in which the chemical and short-range effects are given prominence. It is therefore proposed that the valence bond view of solids be resurrected. How this may work and some of its implications are illustrated below.

Basically we are going to make a chemist's ball-and-stick model of solids. We begin with a simple $2 \times n$ planar lattice of monovalent balls

and connect them with sticks

Each of the several ways to connect the atoms represents a possible wavefunction for the electronic ground state of the solid. These all should have the same energy, and they are not in general symmetry functions for the translation symmetry group of the solid. The actual wavefunction may be a linear combination of these "resonance" structures. The degeneracy of the individual structures is lifted by their interactions. We may think of this as producing a narrow band of many-electron states



Let us now classify the various types of solids by this model of resonating bonding structures:

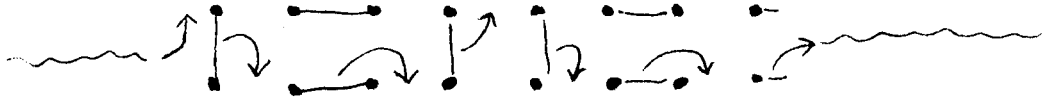
Metals typically have many equivalent nearest neighbors, so that they will have insufficient valence to form bonds with all of them simultaneously. This means that there will be many degenerate bonding structures depending on which of its neighbors each atom bonds to.

Semiconductors such as silicon typically have exactly as many nearest neighbors as covalent bonds. There is only one bonding structure in the absence of excitations or impurities.

Molecular solids such as solid hydrogen similarly have nondegenerate bonding structure.

Ionic solids have no bonds at all.

What I am getting at is the nature of conduction. An interesting illustration of what is going on is given by a comparison of diamond and graphite. Diamond with only one structure is an insulator. Graphite, which has many equivalent resonating structures, is a conductor. I propose to look at conduction as the flipping of bonds



the change from one resonating structure to another.

To see whether I am on the right track, I would like to evaluate numerically from scratch the resistance of some solid. This desire is thwarted by a number of conceptual difficulties. Principal among these is the fact that the resistance of metals is dominated by interactions of the electrons with the vibrations of the lattice. A simpler problem would be to look at the effect on conduction due to individual atoms. That leads us to look at the increased resistivity in dilute alloys with

noble metal hosts, which is a rather well-studied area experimentally.

Linde[3] in his studies of dilute alloys found a very interesting dependence on the valence of the impurity atom. Elements that lie to the right of copper (Ag, Au) in the periodic chart, when dissolved in copper (Ag, Au) produce an increased resistance proportional to the square of their distance to the right (see Fig. 1). That means that the resistance is proportional to the square of the difference in valence. Now above we said that the conduction was due to the interchangeability of the equivalent resonance forms. The bonds flip in the direction of conduction. An impurity atom with a valence greater than that of the host will tie down several of the bonds that were to have been used in making resonance structures. More importantly, when the bonds are flipping during conduction, the bonds forms by the impurity will eliminate certain of the conduction paths that otherwise could have been used. The dependence on valence is now natural. That it should be quadratic is not surprising (but I have not yet explained it completely).

The transition metals are more stubborn. As we can see from Fig. 1, they do not give such a simple quadratic behavior. The solution must be that the effective valence is not given merely by the distance away from copper. Of course the number of electrons available for bonding changes by one for each step removed from copper. Some of these electrons are involved in bonds with the host copper. Some remain localized on the transition metal atom. These nonbonding 3d electrons may be magnetic and could be counted in that way.

To find the number of nonbonding electrons we would look at the

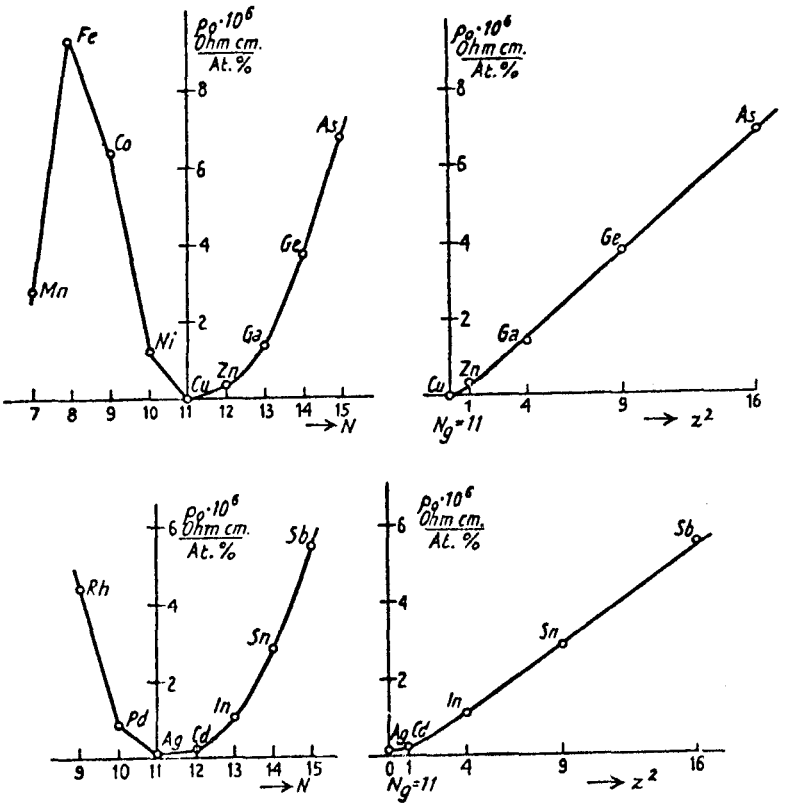


Fig. 1. Increase in the resistance of copper due to one atomic per cent of various metals in solid solution. N denotes the number of electrons outside an inert gas shell; z denotes (N - 11), from Ref. 4.

magnetic moment of dilute paramagnetic alloys. This is complicated by a number of difficult effects. Among them are temperature-dependent interactions between the localized magnetic moments and the conduction electrons, and crystal-field spin-orbit effects. But the magnetic data available (such as that of Hildebrand[5]) seem to indicate, for instance, that manganese has most of its electrons involved in its localized moment, few left for bonding, and hence has a small effect on the resistance. The opposite is true for iron.

This much recommends at least a more complete study of the literature to (1) verify and to characterize the valence dependence of resistivities, (2) to explain in terms of valence the magnetic properties of alloys, such as the Kondo effect, and (3) develop the implications of the valence bond view of solids to the properties such as specific heat, thermoelectric power, and magnetoresistance. Of practical interest will be the applications to semiconductors and superconductors, both of which seem to me to be conspicuously susceptible to a valence bond treatment. Of course there are many calculational details to work out, but they will yield.

References

1. Disclaimer: much of the background supplied in this proposition is not original to me, but the potentialities have not been developed. This proposition serves mostly to emphasize the plausability of the approach. This will be my field of research for at least the next year.

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