Theoretical Studies of Photoionization

Thesis by
Marco A.C. Nascimento

In Partial Fulfillment of the Requirements
for the Degree of Master of Sciences

California Institute of Technology
Pasadena CA 91125

(Submitted June 15, 1976)

Table of Contents

Abstracts

The photionization cross-section is shown to be directly related to the imaginary part of the frequency dependent polarizability.

Using this relation, an approximate representation of the frequency-dependent polarizability is contructed from a discrete set of transition frequencies and oscillator strengths, which in turn is used in an analytical continuation procedure for complex values of the frequency. The great advantage of the method resides on the fact that the use of a discrete repreentation for the dynamic polarizability explicitly avoids the use of continuum functions.

The method is applyed to the calculation of the photoionization cross-section for the $2\,^1S$ and $2\,^3S$ metastable states of the He atom and for the H^- atom. Further improvements of the technique are suggested.

Section I

The importance of photoionization processes

When electromagnetic radiation interacts with a system of atoms or molecules, several processes may occur depending on the energy of the incident photons relative to the energy states of the system.

For atoms[1] the most common processes are photoexcitation and photoionization, where the system is left in an excited state by absorption of the photon, or in case the photon energy is higher than the ionization potential, in a continuum state, since in this condition the excess of energy can be removed as kinetic energy of the electron. Photoionization occurs in general from excitation of valence electrons to the continuum. Another process can occur leading to photoionization of the atom. Sometimes it is possible that the photon energy is high enough to excite inner shell electrons. These excited states can be mixed with continuum states of other terms lying in the same energy region. In this case a radiationless transition from the discrete to the continuum state may occur. The process is known as autoionization or pre-ionization. Autoionization in polyelectronic atoms may take place also as a result of double excitation. In this process two electrons are excited simultaneously to higher energy states. When the excitation energy of the two electrons exceeds the first ionization potential, the atom may undergo a radiationless transition in which one of the excited electrons falls into a lower state, the de-excitation energy being used to eject the other electron from the atom.

For molecules[2,3] the situation is much more complicated due to the greater number of open channels. The most common processes for atoms and molecules are summarized in Table I.1.

When the system (atom or molecules) is a negative ion the photoionization process is called photodetachment.

Photoionization studies are important in many respects. For instance, photodetachment provides a precise method for determining electron affinities as well as photoionization to determine ionization potentials. The knowledge of the photodetachment cross-section for a given system permits the calculation for the reverse process, i.e., the process of electron attachment to a neutral atom or molecule. Both processes are very important in monoatomic gases at low pressures.

Maybe one of the most important aspects related to these phenomena is the study of the structure of the ionosphere, by definition, the part of the earth's atmosphere in which free electrons exist in sufficient number to have an important effect on the travel of radio waves.[4,5,6] The free electrons produced when the earth's atmosphere is photoionized by solar radiation, have a peak concentration at heights near 250 Km. Of course the distribution of the free electrons with height depends on the gas composition of the atmosphere with height, and in the ability of the gases, in each region, to suffer photoionization and the reverse process, electron capture. Then, to understand the structure of

Table I.1

PHOTON-MATTER INTERACTION PROCESSES

$X + h\nu \rightarrow X^*$	Atomic excitation
$X + h\nu \rightarrow X^+ + e^- + \mathrm{KE}$	Atomic photoionization
$X + h\nu \rightarrow X^* \rightarrow X^+ + e^- + \mathrm{KE}$	Autoionization
$XY + h\nu \rightarrow XY^*$	Molecular excitation
$XY + h\nu \rightarrow X + Y + \mathrm{KE}$	Molecular dissociation
$XY + h\nu \rightarrow X^* + Y + \mathrm{KE}$	Molecular dissociation
$XY + h\nu \rightarrow X + Y^* + \mathrm{KE}$	Molecular dissociation
$XY + h\nu \rightarrow X^* + Y^* + \mathrm{KE}$	Molecular dissociation
$XY + h\nu \rightarrow XY^* \rightarrow X + Y + \mathrm{KE}$	Predissociation
$XY + h\nu \rightarrow XY^+ + e^- + \mathrm{KE}$	Molecular photoionization
$XY + h\nu \rightarrow XY^* \rightarrow XY^+ + e^- + \mathrm{KE}$	Preionization

the ionosphere it is of fundamental importance to know the rates for these processes for different frequencies of the incident radiation. That is, photoionization, photodetachment and electron-attachment cross-sections are quantities of fundamental importance in these studies.

In terms of distribution of electrons the ionosphere is divided in layers, determined by relative maxima of the electron distribution. Those distributions that occur near heights of 100, 170 and 250 Km. are said to belong to the E layer (sometimes called F), F_1 layer and F_2 layer, respectively. The part of the ionosphere below 90 Km is called the D region. For the composite F layer it seems that the major components are O and N_2. For the region D the ion chemistry seems to be largely controlled by O, O_3, NO, NO_2, CO_2, H_2O and alkali metals present only in very small proportions. So, at least for these compounds and their ions, the knowledge of good cross-sections is very important.

At higher altitudes H and He become the predominant components.

Another important subject connected with these processes is astrophysics. To give just one single but important example, it was suggested,[7] and it now seems to be accepted, that the continuum absorption of H^- is mainly responsible for the opacity in the visible and infra-red spectra of stellar atmospheres. That is why this ion has been the subject of many calculations and experiments.

Of course, when good experimental values of the cross-sections for a given system are known, they can be used to test new theoretical models. And once a good theoretical model is developed it can be useful to determine the cross-sections for important processes of difficult experimental investigation.

The main objective of our work is to try to develop one such a method. In section II we will describe the methods which have been used for this purpose, and which are extremely laborious methods. Then we will present an alternative method and some of its applications.

References

1. G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York, 1945, 2nd edition.
2. G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand Reinhold Co., New York, 1950, 2nd edition.
3. G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co. Inc., New Jersey, 1967.
4. J. A. Ratcliffe, "An Introduction to the Ionosphere and Magnetosphere," Cambridge University Press, 1972.
5. J. A. Ratcliffe and K. Weekes in "Physics of the Upper Atmosphere," edit. J. A. Ratcliffe, Academic Press, New York, 1960, page 378.
6. R. M. Goody, "Atmospheric Radiation," Oxford University Press, London, 1964.
7. R. Wildt, Astrophys. J., 89, 295 (1939).

Section II

Theoretical Description of Photoionization Processes

1. Basic Definitions

While we are dealing exclusively with photoionization processes, the definitions below are of general applicability, being used in connection with any kind of scattering process (photons, electrons, neutrons, α-particles, etc.).

Consider a beam of monochromatic photons directed toward a scattering target, which can be an atom or molecule. After impact, if the photon energy is high enough to ionize the atom or molecule, electrons will be ejected in all directions and can be detected by methods to be sketched in Section III.

Referring to Figure II. 1, let us define a polar system of coordinates with origin at the scattering center and with the polar axis (z-direction) being the direction of the incident beam. Let us now assume a detector located at P (characterized by the polar coordinates r, θ, φ) subtending a cone of a solid angle $d\Omega$ at the origin. We now define the "differential cross-section" $\sigma(\theta, \varphi)$ as the ratio of the scattered electrons at the detector per unit angle solid and of the flux of incident photons. Thus,

$$\sigma(\theta, \varphi) \equiv \frac{d\sigma}{d\Omega} = \frac{I(\theta, \varphi)}{I_0} , \qquad \text{(II. 1)}$$

where I_0 is the number of photons incident from the left per unit surface and unit time and $I(\theta, \varphi)$ is the flux of scattered electrons through the cone subtended by the detector. From the definition of (II. 1), we see that $\sigma(\theta, \varphi)$ has dimensions of an area.

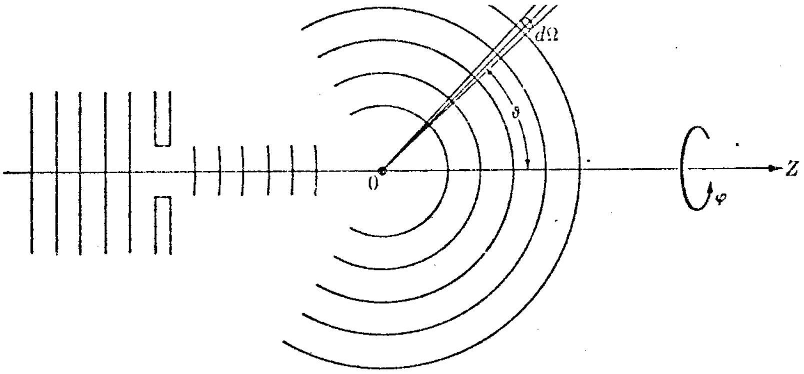


Fig.II.1

The "total cross-section" for the process is defined as the total number of electrons ejected per unit time divided by the incident flux, which can be calculated from (II. 1),

$$\sigma = \int \sigma(\theta, \varphi)\, d\Omega = \int_0^{2\pi} \int_0^{\pi} \sigma(\theta, \varphi) \sin\theta \, d\theta \, d\varphi \ . \tag{II. 2}$$

The calculation of this quantity and its dependence on the incident photon energy are the main objectives of our present work.

2. Expressions for the Total Cross-Section

Consider an atomic or molecular system in an initial state i, having an energy E_i. Consider processes in which the system absorbs a photon making a transition to a state f in which one of its electrons is free. The set of all states of the system in which one electron is free and the residual system is in a state of definite energy is called a continuum of the system.

The quantum-mechanical expression for the cross-section for absorption of photons of frequency ν, accompanied by such a transition, is, in the dipole approximation:

$$\sigma(\nu) = \frac{8\Pi^3 \nu}{3c} \frac{1}{g_i} \sum_i \sum_f \left| \int u_f^* \sum_\mu c_\mu r_\mu u_i \, dv \right|^2 \tag{II. 3}$$

In the above expression u_i are the wave functions of the g_i-fold degenerate initial state of the system, $\sum_i$ denoting the sum over all g_i of these states. The functions u_f are continuum eigenfunctions of the energy, belonging to the eigenvalue Ei+hν and, for this expression, they are in energy normalization, i.e.,

$$\int u_{f_A}^{*} u_{f_B} \, dv = \delta(E_A - E_B) \, .$$

Other kinds of normalization for the continuum wave functions are often used, with corresponding modifications in the multiplying factor in (II.3). Expression (II.3) is derived in Appendix I, where a brief discussion of the normalization for continuum wave functions is also presented. $\sum\limits_{f}$ denotes summation over all the continuum states to which transitions are energetically possible.

When u_f and u_i are exact solutions of the Schroedinger equation for the system, the dipole matrix element can be transformed into two other equivalent expressions commonly referred to as dipole velocity and dipole acceleration matrix elements. The usual expression is called dipole length matrix element.

$$M = \int u_f^{*} \sum_{\mu} r_{\mu} u_i \, dv \qquad \text{(dipole length)} \qquad \text{(II. 4)}$$

$$= (1/h\nu) \int u_f^{*} \sum_{\mu} \nabla_{\mu} u_i \, dv \qquad \text{(dipole velocity)} \qquad \text{(II. 5)}$$

$$= (1/h\nu)^2 \int u_f^{*} \sum_{\mu} \vec{r}_{\mu}/r_{\mu}^{3} \, u_i \, dv \qquad \text{(dipole acceleration)} \qquad \text{(II. 6)}$$

The equivalence among these expressions can be derived using the commutation relationship (see Appendix I).

$$[\hat{r}, \hat{H}] = \frac{i\hbar}{m}\hat{p} \qquad \text{(II. 7)}$$

The importance of these equivalent expressions lies in the fact that, because exact wave functions are in general not known, we are forced to use approximate ones, for which these expressions are not equivalent anymore. Then, the results obtained by the use of each one of these expressions will reflect the ability of the approximate wave functions to describe the phenomenon in different regions of the space. For instance, in the dipole length the integrand is most important for large values of r_μ, while the dipole acceleration is most important for small values of r_μ. The dipole velocity expression will be most important for intermediate values of r_μ. Most of the calculations for two-electron systems used variational Hylleraas type wave functions, which are most reliable for r_μ of the order of the atomic radius, but are poor approximations for very large or very small values of r_μ. In such cases, we should expect the dipole velocity expression to be the most accurate of the three forms. This fact has been confirmed in some calculations.

There is another important way of expressing the cross-section. It can be shown that the oscillator-strength for a given transition is related to the absorption coefficient, $k(\nu)$, by the relation[1]

$$f_n = \frac{mc}{\pi N e^2} \int_n k(\nu)\, d\nu \qquad \text{(II. 8)}$$

i.e., f is directly proportional to the area under the absorption band, N being the number of atoms per cm^3. Now, since $k(\nu) = N\sigma(\nu)$, we can write:

$$f_n = \frac{mc}{\pi N e^2} \int_n \sigma(\nu) N d\nu \qquad (II.9)$$

which, by differentiating gives:

$$\frac{df}{d\nu} = \frac{mc}{\pi e^2} \sigma(\nu) ,$$

or, since $hd\nu = dE$, and expliciting $\sigma(\nu)$, we have:

$$\sigma(\nu) = \frac{\pi h e^2}{mc} \frac{df}{dE} \qquad (II.10)$$

Expression (II. 20) is important firstly because it enables us to treat the photoabsorption cross-section and the spectral density of oscillator-strengths as asynonymous; secondly, because it provides a good test for the theoretical values of $\sigma(\nu)$, since the oscillator-strength sum rule must be satisfied:

$$\sum_n f_n + \frac{mc}{\pi e^2} \int_{\nu_0}^{\infty} \sigma(\nu) d\nu = N_e \qquad (II.11)$$

where N_e is the number of electrons of the system and $\sum_n f_n$ indicates the summation over the discrete part of the spectrum. Following this criteria, Dalganno and Kingston[2] were able to show that the theoretical values for $\sigma(H^-)$ calculated by Chandrasekhar[3] should be in error, since they violated the sum-rule (II. 11).

3. General Methods for Calculation of σ

The problem of calculating the photoionization cross-section lies in the calculation of the matrix elements in (II. 3). Of course, for its calculation, we need to specify the initial and final states of the system. So, the methods of calculation differ, basically, on the choice of the bound and continuum states. We proceed with a brief summary of these methods. More details can be found in the reviews by Ditehburn and Öpik,[4] Branscomb,[5] Stewart,[6] the books by Marr[7] and Christophorou,[8] and the references cited during the discussion.

The only exact soluble systems are hydrogen-like atoms, for which the Schroedinger equation can be solved for the bound and continuum states. For any other system, approximate methods have to be used to obtain the initial and final states. For the bound states of two- and three-electron atoms, there are very accurate wave functions, which have been extensively used for calculations in He, H^-, and Li. For other systems, application of some of the methods described below must be made.

3a. Central Field Approximation Methods

In the central field approximation[9] for many electron systems, the wave functions for the individual electrons are separated and can be expressed in the following form, using spherical coordinates:

$$u_b = \left[\frac{(2\ell+1)}{4\pi} \cdot \frac{(\ell-m)!}{(\ell+m)}\right]^{\frac{1}{2}} R_{n,\ell}(r)\, P_\ell^m(\cos\theta)\, e^{im\phi} \qquad \text{(II. 12)}$$

for a bound state and

$$u_f = \sum_{\ell=0}^{\infty} (2\ell+1)\, i^\ell\, e^{i\delta_{E,\ell}}\, R_{E,\ell}(r)\, P_\ell(\cos\theta) \qquad \text{(II. 13)}$$

for a free state. In the expression for u_f, $\delta_{E,\ell}$ represents the phase-shift for the partial wave ℓ, which depends on the energy and is determined uniquely by the differential equation for $R_{E,\ell}$ and the requirement that R be regular at the origin. For the bound states, the radial wave functions are normalized to unity,

$$\int_0^\infty R^2_{n,\ell}\, dr = 1$$

and for the free states, it is such that the asymptotic behavior is given by:[10]

$$R_{E,\ell} \sim \frac{1}{k_r} \sin\left[k_r - (\tfrac{1}{2})\ell\pi + \delta_{E,\ell}\right] \qquad \text{(II. 14)}$$

where $\delta_{E,\ell}$ may contain Coulomb and non-Coulomb shifts. In (II. 14), $k = mv/\hbar$ where v is the velocity of the ejected electron.

Now, suppose we are dealing with an atom for which the LS coupling is a good approximation; and let us characterize the initial and final states by the set of quantum numbers SLM_LM_S and $S'L'M_L'M_S'$.

In order to obtain an expression for the cross-section in terms of (II. 12) and (II. 13), we note that, since the dipole moment operator is spin independent, the LS coupling selection rules apply:

$$S = S'; \quad M_S = M_S'; \quad L = L',\ L' \pm 1; \quad M_L = M_L',\ M_L' \pm 1$$

In addition, since the dipole moment is a one-electron operator, there will only be matrix elements between the states directly involved in the process. Calling "passive" the electrons not involved and "active" the involved ones, introducing expressions (II. 12) and (II. 13) in (II. 3) gives, after integration over angular coordinates:[11]

$$\sigma(\nu) = A \prod_{\substack{\text{passive}\\\text{electrons}}} \left| \int_0^\infty R^i_{n,\ell} R^f_{n,\ell}\, r^2 dr \right|^2 \cdot$$

$$\left\{ C_{\ell-1} \left| \int_0^\infty R^i_{n,\ell} R_{E,\ell-1} r^3 dr \right|^2 + C_{\ell+1} \left| \int_0^\infty R^i_{n,\ell} R^f_{E,\ell+1} r^3 dr \right|^2 \right\}_{\substack{\text{active}\\\text{electrons}}}$$

where A is a constant which depends on the incident photon frequency, ν, and $C_{\ell-1}$ and $C_{\ell+1}$ are constants which depend on the spectroscopic type of the initial and final states. Bates[11] presented tabulated values of these constants.

The problem now lies in the calculation of the integrals

$$\int_0^\infty R^i_{n,\ell}\, R^f_{n,\ell}\, r^2\, dr \qquad \begin{matrix}\text{passive}\\\text{electrons}\end{matrix}$$

$$\int_0^\infty R^i_{n,\ell}\, R^f_{E\left\{\begin{matrix}\ell-1\\ \ell+1\end{matrix}\right.}\, r^3\, dr \qquad \text{active electrons}$$

The integral over the passive electrons can be looked at as a measure of the core distortion caused by the ejected electron. These integrals will be close to unity if the core is slightly distorted and equal to unity in a frozen-core approximation. They are not difficult to evaluate. Integrals involving active electrons are the real problem. For their calculation several approximations have been used for the bound and free wave functions. Simple Hartree wave functions have been used,[12] but in some cases effects of exchange and polarization have been considered.[13] The main fact that came out from these different calculations is that the integral over active electrons is very sensitive to the choice of the states involved, which makes its calculation much more difficult. We will now discuss briefly some systematic ways of getting continuum wave functions.

3a. 1. Hartree-Fock Treatment of Initial and Final States

The Hartree-Fock scheme[14] provides a systematic way of getting equations to be solved for bound states. These are obtained by taking an anti-symmetric orbital product for the total wave function and then applying the variational principle to minimize the energy. The resulting equations determine the optimum one-electron orbitals. For bound states the systematics have been known since the work by Fock in 1930.[15]

The application of the Hartree-Fock scheme to the calculation of continuum states was first rigorously developed by Seaton in 1953,[16] and first applied by him to the study of electron excitations of the ground configuration terms of oxygen. It was shown by Seaton[16] that the most consistent and general way of obtaining continuum Hartree-Fock solutions is by applying the variational principle on an explicitly anti-symmetric product wave function of N one-electron orbitals (obtained self-consistently in a separate calculation) and a continuum orbital, the equation for which is determined by substituting the total wave function into the N+1-electron Schroedinger equation. Then, following Seaton, let us define the total Hamiltonian for the N+1 electrons by

$$H = H_i + H_{(i-1)} + \sum_{\substack{j=1 \\ (j\neq 1)}}^{N} \frac{1}{r_{ij}}$$

where

$$H_i = -\tfrac{1}{2}\nabla_i^2 - \frac{Z}{r_i}$$

$$H_{(i-1)} = \sum_{j=1}^{N} (-\tfrac{1}{2})\nabla_j^2 - \sum_{j>k}^{N} \frac{1}{r_{jk}}$$

The wave function which has already been determined is denoted by:

$$\psi_n^{(i-1)} = \psi_n(x_1, x_2, \ldots, x_{i-1}, x_{i+1}, \ldots, x_N)$$

The total wave function is then expressed as:

$$\Psi = \sum_{n} A\, \psi_n^{(i-1)}\, \phi_n(i) \qquad \text{(II. 15)}$$

where the summation is over the complete set of states of the core system. As long as only electrostatic interactions are considered, the angular momentum of the whole system is conserved. Then, if we denote the states of the total system by $L^T S^T M_L^T M_S^T$, each piece of the expansion (II. 15) can be written:

$$\psi_n(L^c S^c M_L^c M_S^c | i-1)\, \phi_n\, (k\ell\ m_\ell\ m_s | i)$$

such that the coupling gives the total angular momentum of the given state of the whole system. Then, expression (II. 15) can be rewritten:

$$\Psi(L^T, S^T, M_L^T, M_S^T) = A \sum_{n,\nu} C_\nu \psi_n(L^c, S^c, M_{L_\nu}^c, M_{S_\nu}^c | i-1) \cdot$$

$$\cdot\ \phi_n\ (k\ell\ m_{\ell_\nu}\ m_{s_\nu} | i) \qquad \text{(II. 16)}$$

where C_ν are the Clebesch-Gordon coefficients for the coupling. Now, remember that ϕ_n can be written in terms of an angular and radial part

$$\phi \sim Y_\ell^m(\theta, \varphi)\, \frac{1}{r}\, F_{k\ell}(r)$$

Now, if we assume that Ψ is the exact solution for the continuum, we can write:

$$[H - E]\, \Psi = 0$$

and substituting the expression (II. 15) for ψ, multiplying both sides by ψ_m^* and integrating over all coordinates except for dr_i, we get the differential equation satisfied by the radial part of ϕ which has the form:

$$\left\{ \frac{d^2}{dr^2} + k_i^2 - \left[\frac{\ell i(\ell i+1)}{r^2.}\right] \right\} F_i(r) = \sum_j V_{ij}(r)\, F_j(r) \qquad \text{(II. 17)}$$

In (II. 17), V_{ij} contains direct and exchange interactions and is, in general, quite complicated. For details of the derivation of the coupled equations (II. 17) and for expressions for V_{ij} for different electronic configurations, the reader is referred to the papers by Seaton[16] and Percival and Seaton.[17] A simple case, the electron scattering by a hydrogen atom, is treated very clearly by Moiseiwitsch.[18]

3a. 2 Close-Coupling Approximations[6,7,19,20]

Basically, the close-coupling approximations are obtained by truncation of the expansion (II. 15). With this truncation, it is hoped that the continuum states of the total system can be well described by a finite number of the core states. That is, only the remaining terms will be closely-coupled. The nomenclature varies from author to author. For instance, Burke and Smith[21] in their review of low-energy scattering of electrons by hydrogen atoms, classified the various coupling treatments as follows:

a) static approximation - when only 1S state of the hydrogen atom was considered in the expansion

(II. 15). In this case, the radial equation uncoupled and reduced to only one equation of the form (II. 17).

b) strong-coupling approximation - when any two S states, for instance 1S and 2S of the hydrogen atom, are considered in (II. 15). In this case, there are two coupled radial equations to be solved.

c) close-coupling approximation - when other than S states are added in the expansion (II. 15).

The convergence of the close-coupling approximation has been investigated by Burke[22] for different systems.

3a. 3 Polarized Orbital Approximation[6, 7]

In this approximation, an attempt is made to take into account the interaction between the continuum electron and the core. This is done by adding to the core wave function a polarization term such that the new core function is written:

$$\psi_{core} = \psi^{o}_{core}\,(i-1) + \psi_{pol}$$

where ψ_{pol} is a function of the N+1 electrons and this expression is inserted in (II. 15). This method was proposed by Tamkim,[23] who derived a method of getting ψ_{pol}. The method has been applied by him and others, and in certain cases the results are better than the ones obtained with close-coupling.

Another way of taking core polarization into account was suggested by Bates[24] in his calculation of photodetachment of atomic potassium. The same approximation was used by Klein and Brueckner[25] for O^-. Instead of trying to get the continuum wave functions for the total system, the equation for the continuum electron is solved in the field of the core (exchange neglected) and a term is added to the potential to allow core polarization:

$$V_p = -\frac{1}{2} \frac{\alpha}{(r^2 + \rho^2)^2}$$

where α is the polarizability of the core and ρ is the core radius. Both parameters can be calculated or used as semi-empirical quantities to be varied to reproduce experimental results.

3a. 4 Correlated Orbitals Approximation[6, 7]

In this approach, the interaction between the continuum electron and core is fully accounted for by using a wave function which explicitly depends on the inter-electronic distance r_{ij}. Of course, there is little hope for the application of this approach to large systems, while it has been successfully applied to the calculation of photodetachment of H^- by Geltman.[26]

3. b. Quantum-Defect Method[6, 7]

This is a general approach designed to calculate the asymptotic behavior of continuum functions and corresponding phase-shifts. It can be shown, by means of a partial wave analysis, that the scattering amplitude, which is directly related to the cross-section, is a function of the phase shift (difference between the phases of the incoming and scattered waves).[27] Then, if a procedure to determine this phase-shift is found, we can calculate the cross-sections. This approach was developed by Seaton[28] and applied to the calculation of photoionization cross-sections by Burges and Seaton.[29] It was discussed in Section (II. 1) that in the dipole length approximation, the larger contributions for the transition moment come from large values of r, where the potential can be taken as nearly Coulombic. The radial equation for the active electron can be written:

$$\left[\frac{d^2}{dr^2} - \frac{\ell(\ell+1)}{r^2} + E - v(r)\right] R(E,\ell|r) = 0 \qquad \text{(II. 18)}$$

where $v(r) = -2Z/r$ for small r and $= -2Z'/r$ for large r, E being the effective nuclear change. The bound states ($E < 0$) occur for discrete values of $E = E_{n,\ell}$ and can be related to the experimentally observed Rydberg series by the relation

$$E_{n,\ell} = \frac{-Z'^2}{n'^2_\ell}$$

where n' is the effective quantum number. This permits us to define a quantum defect by

$$\mu_{n\ell} = n - n'_\ell \qquad \text{(II. 19)}$$

which tends to zero in the limit of a pure Coulombic field. Now, for the continuum states ($\epsilon = k^2 > 0$), the solution of (II. 18) has the following asymptotic form:[28]

$$R(k^2, \ell | r) \sim \left\{ G_\ell^c(\epsilon, r) \cos \delta_\ell - H_\ell^c(\epsilon, r) \sin \delta_\ell \right\}$$

where δ_ℓ is the additional shift due to the departure from an exact Coulomb field, and G_ℓ^c and H_ℓ^c are the respective regular and irregular solutions of the wave equation for motion in a Coulomb field, which have the asymptotic form:

$$\begin{matrix} G_\ell^c \\ \\ H_\ell^c \end{matrix} \sim \begin{matrix} \sin \\ \\ \cos \end{matrix} \left[kr - (\tfrac{1}{2})\ell\pi - \alpha \ln (2kr) + \eta e \right]$$

where $\alpha = Z'/k$.

In their treatment, Burgess and Seaton[29] chose for the continuum function,

$$R(K^2, \ell | r) = G_\ell^c(\epsilon, r) \cos \delta_\ell + \{1 - \exp(-\delta_\ell Z_r / a_0)\}^{2\ell+1} \cdot$$

$$\cdot \; H_\ell^c(\epsilon, r) \sin \delta_\ell \qquad \text{(II. 19)}$$

where the cut-off factor $\{1 - \exp(\quad)\}^{2\ell+1}$ was included to avoid H_ℓ^c blowing up at small r. Now, it remains to find δ_ℓ, which will define the continuum wave function and will allow the calculation of the cross-section. It is known from the theory of the variation of phase-shifts with energy, for low energies of the incident particle, that:[30]

$$\lim_{k \to 0} k^{2\ell+1} \operatorname{cotg} \delta_\ell \to \text{const.}$$

So, a relation might be established between the phase-shift and the quantum-defect for quasi-continuum states of the system, i.e., when $n \to \infty$. Seaton[28] was able to show that this relation exists and that:

$$\lim_{n \to \infty} \operatorname{cotg} \pi\mu_{n,\ell} = \lim_{k \to 0} \operatorname{cotg} \delta_\ell \qquad \text{(II. 20)}$$

Furthermore, he argued that it was possible to regard $\mu_{n,\ell}$, by analytical continuation, as a function μ_ℓ of the energy k^2, where $-2mk^2/\hbar^2$ is the energy of a bound state. If the function is extrapolated to small positive values of energy, then (II. 20) may be extended to give:

$$\frac{\operatorname{cotg} \delta_\ell (k^2)}{1 - e^{2\pi\alpha}} = \operatorname{cotg} \pi\mu_\ell \qquad \text{(II. 21)}$$

Once μ_ℓ is known for a given k, the phase-shift can be calculated and, consequently, the cross-section.

More recently, Seaton[31] showed that this extrapolation may be carried out most effectively in terms of a function $Y_\ell(k^2)$, which is such that

$$A_\ell(k^2)\, Y_\ell(k^2) = \operatorname{tg}\{\pi\mu(k^2)\}$$

where

$$A_\ell(k^2) = \prod_{s=0}^{\ell} (1 + s^2/\alpha^2)$$

The bound state energies can be regarded as arising from solutions of the equation:

$$\mathrm{tg}\{\pi n'(k^2)\} = -A_\ell(k^2)\, Y_\ell(k^2) \qquad \text{(II. 22)}$$

Besides that, he showed that $Y_\ell(k^2)$ can be expanded in the form:

$$Y_\ell(k^2) = \frac{\sum a_m \; k^{2m}}{\sum b_s \; k^{2s}} \qquad \text{(II. 23)}$$

for both $k^2 \lessgtr 0$. Then, having obtained $\mu(-k^2)$ from spectroscopic data for different values of the total quantum number n, $Y_\ell(-k_n^2)$ is obtained from (II. 22). Using (II. 23), values of a_m and b_s, with small m and s, are obtained which give the best fit to Y_ℓ. Expression (II. 23) is then used for extrapolation for $k^2 > 0$, allowing the calculation of $\delta_\ell(k^2)$ and the cross-section.

3c. Variational Principles[18]

While none of the variational principles cited below have been used to calculate photoionization cross-sections, it is important to note their existence and possible applicability.

Several variational principles have been developed for the calculation of scattering amplitudes and phase-shifts. For scattering amplitudes, there are the variational principles due to Schwinger and to Kohin. For the phase shifts, there are the principles of Hulthe'n, Tamm, Kato and Schwinger. All these variational principles are well described in the book by Moiseiwitsch.[18]

4. An Alternative Approach

Until recently, most of the calculations of photoionization and photodetachment cross-sections have been done with one of the methods described above, sometimes with slight modifications. In a recent discussion of the situation, Fano and Cooper[32] pointed out large deviations between experimental and theoretical results, which could be mainly due to the lack of a good treatment of the multi-electron correlation energy ignored in the Hartree-Fock approximation. The best agreement with experimental was obtained when using correlated wave functions, at least for the bound state. This is the case for He, H^- and Li. The importance of correlation effects are very clear from the work of Amusya, Cherepkov and Chernoysheva.[33] So, it is necessary to develop a scheme to calculate cross-sections where correlation effects are included in a systematic and practical way, so that it can be used for larger atoms and molecules. This is our intention in this paragraph, but first we will write the cross-section in another interesting and useful form.

4.1 The Optical Theorem[34]

We want to comment first that quantum-mechanically a scattering process can be looked at from two different points of view. In the first one, we assume that the incident beam has been switched on a long time ago and the whole system is in a stationary state. In this approach we look to solutions to the Schroedinger equation with asymptotic behavior described by

$$\psi_k(r) \sim e^{ikZ} + f(\theta,\varphi)\,\frac{e^{ikr}}{r}$$

assuming that V(r) has a finite range; that exludes pure Coulomb potentials. If we refer to Fig. II. 1, we see that the asymptotic form is just a superposition of a plane wave of momentum k propagating in Z direction and an outgoing spherical wave with angular amplitude $f(\theta,\varphi)$ and momentum k. In the other approach, the time dependent approach, we consider the interaction between the incident particle and the scattering target as a perturbation which causes transitions from the initial states of the system to the permissible final states. In our case, this perturbation is simply the electromagnetic field of the photon.

In both approaches it is possible to establish a relation between the cross-section for the photoabsorption and the forward scattering amplitude, i. e., $f(\theta,\varphi)$ for $\theta = 0$ and $\varphi = 0$. This relation, known as optical theorem, can be mathematically expressed as:[35]

$$\sigma(\omega) = \frac{4\pi}{k}\, f(0,\omega) \qquad \text{(II. 24)}$$

This result is very general and can be derived classically from the study of scattering waves by "any kind" of obstacle, and in quantum mechanics it can be derived without specifying the type of potential. So, it is really a general result and the name of "optical theorem" appearing in the quantum mechanics books is probably derived from the analogy with the classical case.

Now comes a beautiful and very important result. It can be shown classically[36] that the index of refraction is related to the forward scattering amplitude, f(0), by the expression:

$$n = \sqrt{1 + \frac{4\pi N f(0)}{k^2}} \qquad \text{(II. 25)}$$

where N is the number of atoms per unit volume. Now let us square expression (II. 25) and rewrite it in the following form:

$$n^2(\omega) - 1 = \frac{4\pi N f(0, \omega)}{k^2} \qquad \text{(II. 26)}$$

where (II. 26) now implies the dependence of the index of refraction on the light frequency. Now recall that the index of refraction is defined by the relation:[37]

$$n = \frac{c}{v} = \frac{(\mu_0 \epsilon_0)^{-\frac{1}{2}}}{(\mu\epsilon)^{-\frac{1}{2}}}$$

where c and v are the velocities of the light in free space and in the material, and μ and ϵ are the respective magnetic and electric permitivities. For a non-magnetic material, $\mu = \mu_0$ and

$$n = \left(\frac{\epsilon}{\epsilon_0}\right)^{\frac{1}{2}} \qquad \text{(II. 27)}$$

Both n and ϵ depend on the frequency of the light, but we will not show this dependence until the end of the derivation; just remember. Now, the ratio ϵ/ϵ_0 is by definition the dielectric constant, d, which in turn is related to the electric susceptibility by the relation:[37]

$$d = 1 + 4\pi\chi = 1 + 4\pi N\alpha \qquad \text{(II. 28)}$$

where α is now the electric polarizability. So, squaring (II. 27) and substituting in (II. 28), we get:

$$n^2 - 1 = 4\pi N\alpha \qquad \text{(II. 29)}$$

Now, comparing (II. 29) and (II. 26), we get:

$$f(0, \omega) = k^2\alpha(\omega) \qquad \text{(II. 30)}$$

Substituting (II. 30) in (II. 24), we finally get:

$$\sigma(\omega) = 4\pi k \, I_m \alpha(\omega)$$

or, since $k = \omega/c$

$$\sigma(\omega) = \frac{4\pi\omega}{c} I_m \alpha(\omega) \qquad \text{(II. 31)}$$

That is beautiful. This expression just tells us that to calculate the cross-section at any frequency all we need to know is the polarizability of the system at that frequency, or better its imaginary part. Good. Now, we completely forget about the cross-section and let us think in terms of polarizability and how to calculate its frequency dependence. Quantum-mechanics tell us how to do that. The frequency dependent polarizability is given by:[38]

$$\alpha(\omega) = \sum_{n\neq 0} \frac{f_{no}}{\omega_{on}^2 - \omega^2} + \int_{\epsilon_I}^{\infty} \frac{g(\epsilon)}{\epsilon^2 - \omega^2} d\epsilon \qquad \text{(II. 32)}$$

where f_{no} is the oscillator strength for the transition 0 → n and is given by

$$f_{no} = \frac{2}{3}(E_n - E_o)|\langle 0|d|n\rangle|^2 \qquad \text{(II. 33)}$$

where $\langle 0|d|\rangle$ is the dipole matrix element between the states and in (II. 32) $g(\epsilon)$ are the corresponding oscillator strengths for transitions to the continuum. In (II. 32) the summation is over the discrete states and the integration is over the continuum, ϵ_I being the first ionization potential. But here we are back with the continuum problem again! Equation (II. 31) offers us an alternative, but we did not get rid of the continuum at all! But don't give up, there is still some hope. There is an interesting result that seems to be due to Dalgarno and Lyn[39] which says that if a given distribution of oscillator strengths for a given system satisfies the oscillator strengths sum rule, then it can be used to calculate accurate values of the properties which can be written as sums of oscillator-strengths. This distribution can be "unphysical", but if it satisfies the sum-rule the final answer can be very accurate.

Some attempts have been made to establish a systematic way of getting such a distribution. Our approach is to obtain a distribution of oscillator-strengths using the Random Phase Approximation (from now on abbreviated RPA), which will be briefly described in the next section. This method offers the advantages of furnishing a distribution of oscillator-strengths satisfying the sum rule and of including correlation effects in a practical and systematic way. So, in principle we can calculate the frequency dependent polarizability using a discrete distribution of oscillator-strengths, thus avoiding the continuum states, using the RPA approach. As a matter of fact, a good description of $\alpha(\omega)$ has already been obtained for He and H_2 using this approach.

So, to make effective use of equation (II. 31) we proceed as follows. First, we assume that we have a discrete distribution of oscillator-strengths which gives us a good value of $\alpha(\omega)$,

$$\alpha(\omega) \approx \sum_n \frac{\tilde{f}_{on}}{\tilde{\omega}_{on}^2 - \omega^2}$$

where $\tilde{f}_{on}$ and $\tilde{\omega}_{on}$ are now approximate oscillator-strengths and transition frequencies obtained by the RPA method. The sum over n does not mean that we are summing over the discrete states of the system. It only means that we are trying to replace the summation over all discrete states and integration over the continuum by a finite summation over an approximate distribution. In general, this summation also includes transitions to the continuum. So, the summation includes some bound-bound and bound-free transitions. Now, we extend that to complex arguments writing:

$$\alpha(Z) \approx \sum_n \frac{\tilde{f}_{on}}{\tilde{\omega}_{on}^2 - Z^2}$$

Now, to obtain values of the imaginary part of $\alpha(Z)$ for real arguments, that is, in the real axis, we do the following: we calculate the values of $\alpha(Z)$ for some values of Z in the upper half plane. Then we obtain a set of points $\{\alpha(Z)\}$ in the complex plane. Following this we try to fit these points by some procedure to get an analytical representation of $\alpha(Z)$ in the complex plane. After that, all we need to do is to project it back on to the real axis for values of Z such that $R\ell(Z)$ corresponds to the values of energy which we are interested in and extract the imaginary part of the result. What we get from this is the imaginary part of the frequency dependent polarizability for the real argument, that is $I_m \alpha(\omega)$. Once we have the analytical representation of $\alpha(Z)$, we can do that for as many points as we want and, using (II. 31), we can finally obtain $\sigma(\omega)$. We proceed now with a discussion of how to do this analytical continuation. Figure II. 2 schematically shows the process.

4.2 The Process of Analytic Continuation. Pade' Approximant[40-46]

Basically, the process we use to make the analytical continuation can be divided in five steps. The first step is to obtain a set of oscillator-strengths and transition frequencies using the RPA method. The second step is to choose points in the complex plane where $\alpha(Z)$ is to be calculated. The choise of these points is arbitrary to a certain extent. This can be justified and we will comment about that later. We choose to pick these points in the following way: Let $\omega(I)$ be the $I^{\underline{th}}$ transition frequency. Then we define:

$$\begin{aligned} ZIF &= [\omega(I) - \omega(I-1)]/2 \\ DIF &= [\omega(I) - \omega(I-1)] \cdot FAC \end{aligned} \qquad (II.36)$$

where FAC is an arbitrary factor. Then the points x(I), where the complex polarizability will be calculated, are defined by:

$$x(I-1) = [ZIF + \omega(I-1),\ DIF]$$

The third step is to calculate $\alpha(Z)$ at these points using (II. 35). The fourth step is to fit these points to obtain the analytical continuation. The fifth and last step is using the representation obtained in step four to calculate $\alpha(Z)$ at the real axis, that is $\alpha(\omega)$ $[Z = \omega + i\eta,\ \eta \rightarrow 0]$, and extract its imaginary part. With these last results (II. 31) can be used.

The arbitrary way of choosing the points can be more or less justified by saying that, since $\alpha(Z)$ is analytic in the upper half plane, it has a defined value at any point in that region. Now, if (II. 35) was the true expression, we could develop a Taylor series for $\alpha(Z)$ and a Pade′ Approximant (we shall talk about that later) can be formed from the coefficients of this series. Then, if the Approximant exists, it is unique, since it is uniquely related to the coefficients of the Taylor series. Since (II. 35) is only an approximation to the exact $\alpha(Z)$, we allow the complex part of the points to vary by varying the factor FAC in (II. 36). If we are close to the true representation, the values obtained for small variations of FAC should not differ too much; that is, we try to get a convergence to the true representation of $\alpha(Z)$, by varying the value of FAC.

The method which we used to fit the values of $\alpha(Z)$ is the one described by Haymaker and Schlessinger.[40] The idea is to find a continued fraction such that it is equal to $\alpha(Z)$ at N points x(I).

$$C_N(x) = \frac{f(x_1)}{1+} \; \frac{(x-x_1)a_1}{1+} \cdots \frac{(x-x_N)a_N}{1} \qquad \text{(II. 37)}$$

Requiring that

$$C_N(x_{\ell+1}) = f(x_{\ell+1}) = \frac{f(x_1)}{1+} \; \frac{(x_{\ell+1}-x_1)a_1}{1+} \cdots \frac{(x_{\ell+1}-x_\ell)a_\ell}{1}$$

the coefficients a_N can be calculated by the following recursive algorithm:

$$a_\ell = \frac{1}{(x_\ell - x_{\ell+1})} \left\{ 1 + \frac{(x_{\ell+1}-x_{\ell-1})a_{\ell-1}}{1+} \times \frac{(x_{\ell+1}-x_{\ell-2})a_{\ell-2}}{1+} \cdots \frac{(x_{\ell+1}-x_\ell)a_\ell}{1-[f(x_1)/f(x_{\ell+1})]} \right\} \qquad \text{(II. 38)}$$

and

$$a_1 = \{f(x_1)/f(x_2) - 1\}/(x_2 - x_1) \qquad \text{(II. 39)}$$

We have been talking about Pade′ Approximant and now we are using a continued fraction. But the continued fraction is just a special case of the Pade′ Approximant and is directly related to it; that is, given a continued fraction, it is always possible to find a Pade′ Approximant.[46]

An [M, N] Pade′ Approximant to a given function f(x) is defined by the relation:[46]

$$f(x) \sim [M, N] = \frac{P_M(x)}{Q_N(x)} \qquad (II.\,40)$$

where $P_M(x)$ is a polynomial of degree M and Q(x) is a polynomial of degree N. Unfortunately, this definition is not uniformly used; sometimes people use [M, N] as [N, M] in our definition, so we need to be careful.

Now, one question that could be asked is why we have to use a Pade′ Approximant to fit $\alpha(Z)$. Why not a simple polynomial fitting? The answer is, we don't. But if we want a good representation which can be used to make the continuation, Pade′ Approximants offer the best possible representation. In general, polynomial fittings will not converge to the function when the continuation is made.

There are a lot of interesting results from the theory of Pade′ Approximants; we will quote some of them related to our discussion without any proof or details. Those can be found in the abundant literature that has accumulated in the last ten years, resulting from an increasing use of Pade′ Approximants in many branches of physics.[40-46] From all the reviews, in our opinion, the best one for its clarity is the one by Basdevant.[45] Recently, Baker,[46] who is very active in this field, published a book where the main features of the theory can be found and, contrary to his style, the book is quite clear. Now follows some results. For a given function which has a Taylor series around, for instance, Z = 0 and which converges in a circle $|Z| \le R$. The Pade′ Approximant to this series coverges for $|Z| > R$, while the new radius of convergence cannot always be precise. Then Pade′ Approximants can be used to analytically continue the series outside its circle of convergence. Inside the convergence circle of the Taylor series, Pade′ Approximants usually provide a much better estimate for the function than the series itself, and it accelerates the convergence. Now an important remark. The convergence of the Pade′ Approximant has not yet been formally proved. Even inside the circle of convergence of the Taylor series there is no general proof that its Pade′ Approximant converges. So, it is quite frequent to find quasi-theorems and quasi-corollaries in the theory of convergence of Pade′ Approximants. The convergence is assumed because it is generally observed. Pade′ Approximants can simulate the behavior of a given function f(Z) near its singularities with one or more poles. This is important in connection with the analytical continuation procedure that we used. Another important property of Pade′ Approximants is related to the Stieltjes series,[46, 47] which provides a new way of looking to the problem. The frequency dependent polarizability can be put in terms of a Stieltjes series, and for one such series it can be shown that:

$$[N, N] \geq f(Z) \geq [N-1, N]$$
$$[N, N]' \geq f'(Z) \geq [N-1, N]'$$

So, it is possible to calculate upper and lower bounds for the frequency dependent polarizabilities and related properties. This approach has been explored mainly by Langhoff.[48] For the special case where the function can be represented by a Stieltjes series, it can be shown that there will be a Padé Approximate and that it will converge to the function. This is an important fact again related to the analytical continuation procedure that we used.

4. 3. Applications

We proceed now describing three applications of the scheme described above. We applied it to the calculation of photoionization cross-sections for the metastable states 2^1S and 2^3S of helium and for H^-. The method has also been applied to the photoionization cross-sections of H_2,[49] He[50] and H.[51]

4. 3. 1. 2^1S and 2^3S Metastable States of Helium[52]

The photoionization cross-section of these metastable states below the threshold $n = 2$ has been studied by several authors. In almost all these calculations the bound states were described by Hylleraas or Pekeris-type wave functions, the continuum functions being calculated by the close-coupling approximation.[53-55]

In our calculation we used a simple [12s/8p] contracted set of Gaussian atomic orbitals. The basis set and its specifications are shown in Table II. 1. Now, since for the metastable states we need transition matrix elements between excited states, an approximation was developed to obtain these elements from the set of ground-state - excited-state transitions obtained by the RPA approximation. We will discuss that later. Figures II. 3 and II. 4 show our results compared with two recent calculations by Norcross[54] and Jacobs.[55] The agreement is good and within the experimental uncertainty of ±14% the various calculations agree well with

Table II.1

He (12s/8p) basis set specifications

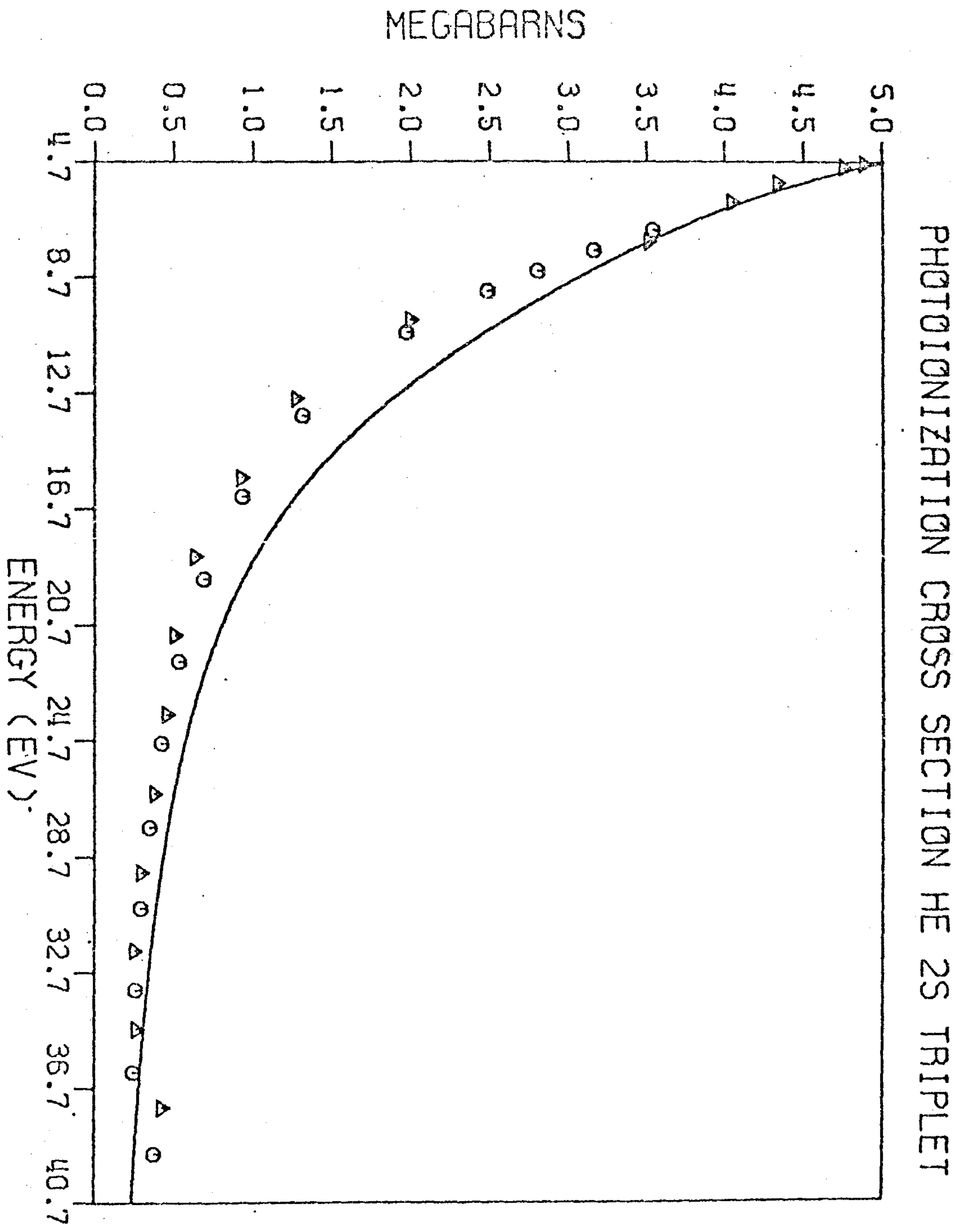
FUNCTION	CENTRE	TYPE	EXPONENT	COEFF.
1	HE	S	3293.6940000	0.0046146
2	HE	S	488.8941000	0.0365754
3	HE	S	108.7723000	0.1978343
4	HE	S	30.1799000	0.8270723
5	HE	S	9.7890530	1.0000000
6	HE	S	3.5222610	1.0000000
7	HE	S	1.3524360	1.0000000
8	HE	S	0.5526100	1.0000000
9	HE	S	0.2409200	1.0000000
10	HE	S	0.1079510	1.0000000
11	HE	S	0.0483700	1.0000000
12	HE	S	0.0216740	1.0000000
13	HE	S	0.0097120	1.0000000
14	HE	S	0.0030000	1.0000000
15	HE	S	0.0010000	1.0000000
16	HE	X	4.5000000	1.0000000
17	HE	X	1.4583690	1.0000000
18	HE	X	0.3462700	1.0000000
19	HE	X	0.1119120	1.0000000
20	HE	X	0.0421630	1.0000000
21	HE	X	0.0170230	1.0000000
22	HE	X	0.0112650	1.0000000
23	HE	X	0.0051045	1.0000000
24	HE	Y	4.5000000	1.0000000
25	HE	Y	1.4583690	1.0000000
26	HE	Y	0.3462700	1.0000000
27	HE	Y	0.1119120	1.0000000
28	HE	Y	0.0421630	1.0000000
29	HE	Y	0.0170230	1.0000000
30	HE	Y	0.0112650	1.0000000
31	HE	Y	0.0051045	1.0000000
32	HE	Z	4.5000000	1.0000000
33	HE	Z	1.4583690	1.0000000
34	HE	Z	0.3462700	1.0000000
35	HE	Z	0.1119120	1.0000000
36	HE	Z	0.0421630	1.0000000
37	HE	Z	0.0170230	1.0000000
38	HE	Z	0.0112650	1.0000000
39	HE	Z	0.0051045	1.0000000

Figure Captions

Fig. II.3 Photoionization cross sections of the $2\,^1S$ state of helium in megabarns. The curve shows the present cross sections obtained by numerical analytic continuation. The triangles and octagons are the calculated results of Norcross (ref.54) and Jacobs (ref. 55) respectively.

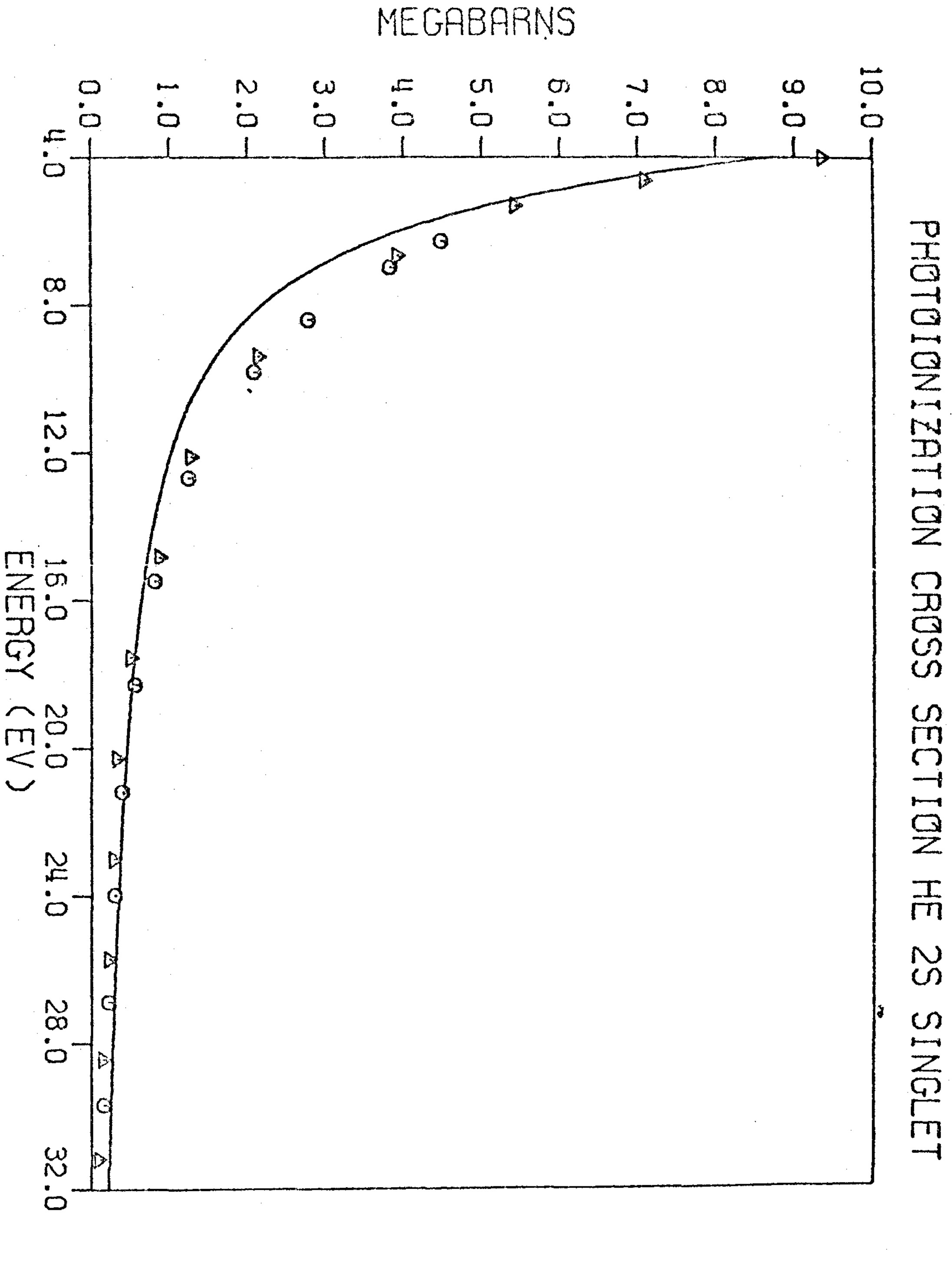
Fig. II.4 Photoionization cross sections of the $2\,^3S$ state of helium in megabarns. The curve shows the present cross sections obtained by numerical analytic continuation. The triangles and octagons are the calculated results of Norcross (ref.54) and Jacobs (ref. 55) respectively.

Fig.II.3


PHOTOIONIZATION CROSS SECTION HE 2S TRIPLET
MEGABARNS
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
4.7
8.7
12.7
16.7
20.7
24.7
28.7
32.7
36.7
40.7
ENERGY (EV)

1·5rf

Fig.II.4


PHOTOIONIZATION CROSS SECTION HE 2S SINGLET
MEGABARNS
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
ENERGY (EV)
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0

experiment.[56] Figures II. 5 and II. 6 show the results obtained for three different values of the factor FAC in (II. 36).

4. 3. 2. Photoionization of H^-

This specie has been extensively studied due to its astrophysical importance. Chandrasekhar[3, 57] and his associates in a series of papers from 1942 to 1958 studied this system using increasingly more accurate two-electron wave functions for the bound state, but using a plane wave approximation for the free state, with exception of the last paper where a Hartree-type wave function was used for the free state. Their results did not show much improvement in going to more accurate bound wave functions and the Hartree-type wave function did not show much improvement over the plane wave approximation. A calculation by John[58] using exchange wave functions for the free-state showed an appreciable improvement. But in the light of experiments by Smith and Burch,[59] all theoretical calculations showed bad agreement with experiments. Another point was the great disagreement among the results calculated using length, velocity and acceleration formulas for the transition moment. Geltman[26] did one of the best calculations using a fully correlated free wave function and a Schwartz 70 parameters bound wave function. The results are in excellent agreement with experiment, if the velocity form is used for the transition moments. This result is also observed by Chandrasekhar. But, contrary to the older calculations, the disagreement among the various forms of transition moment is much smaller in his calculation. The more recent

Fig.II.5

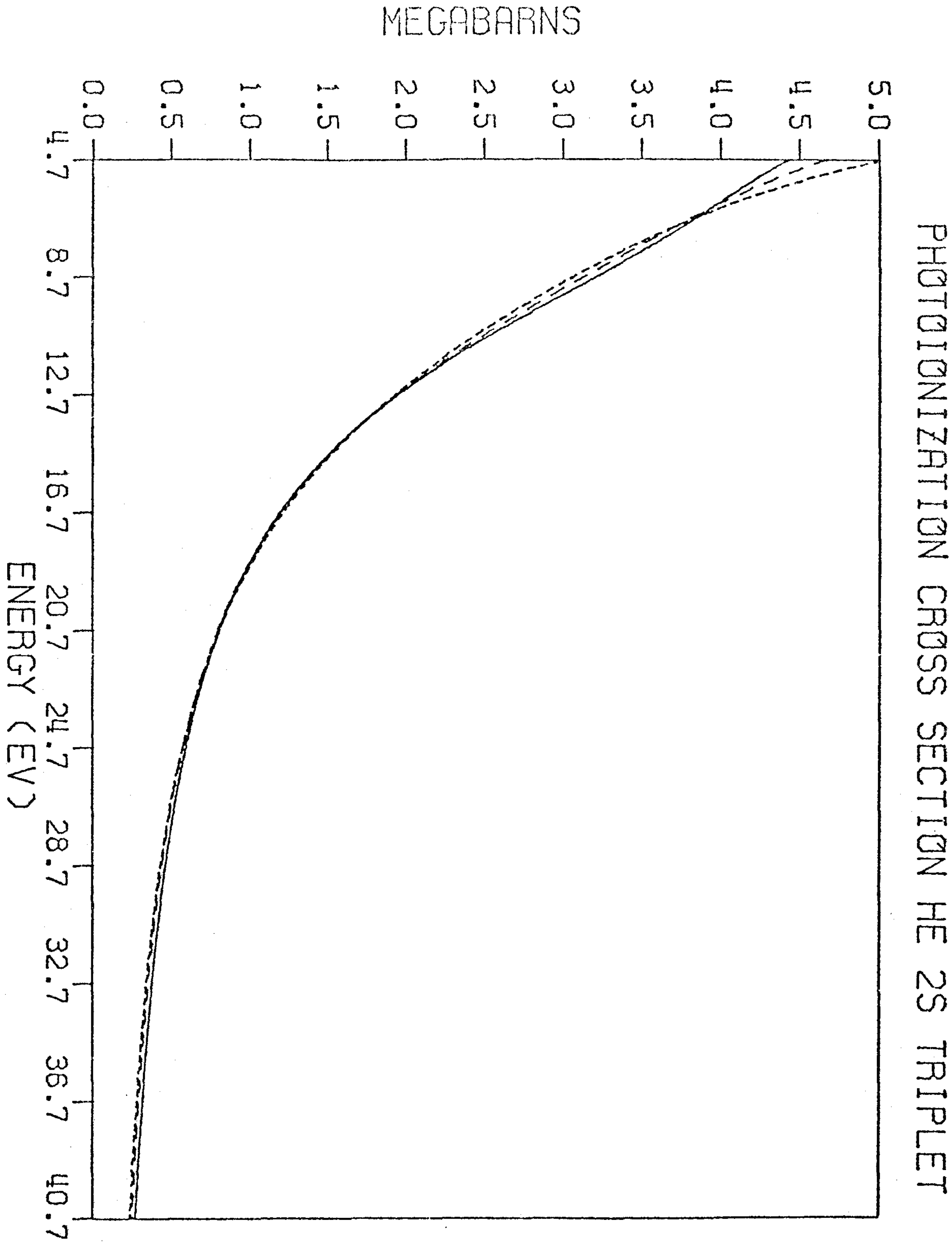
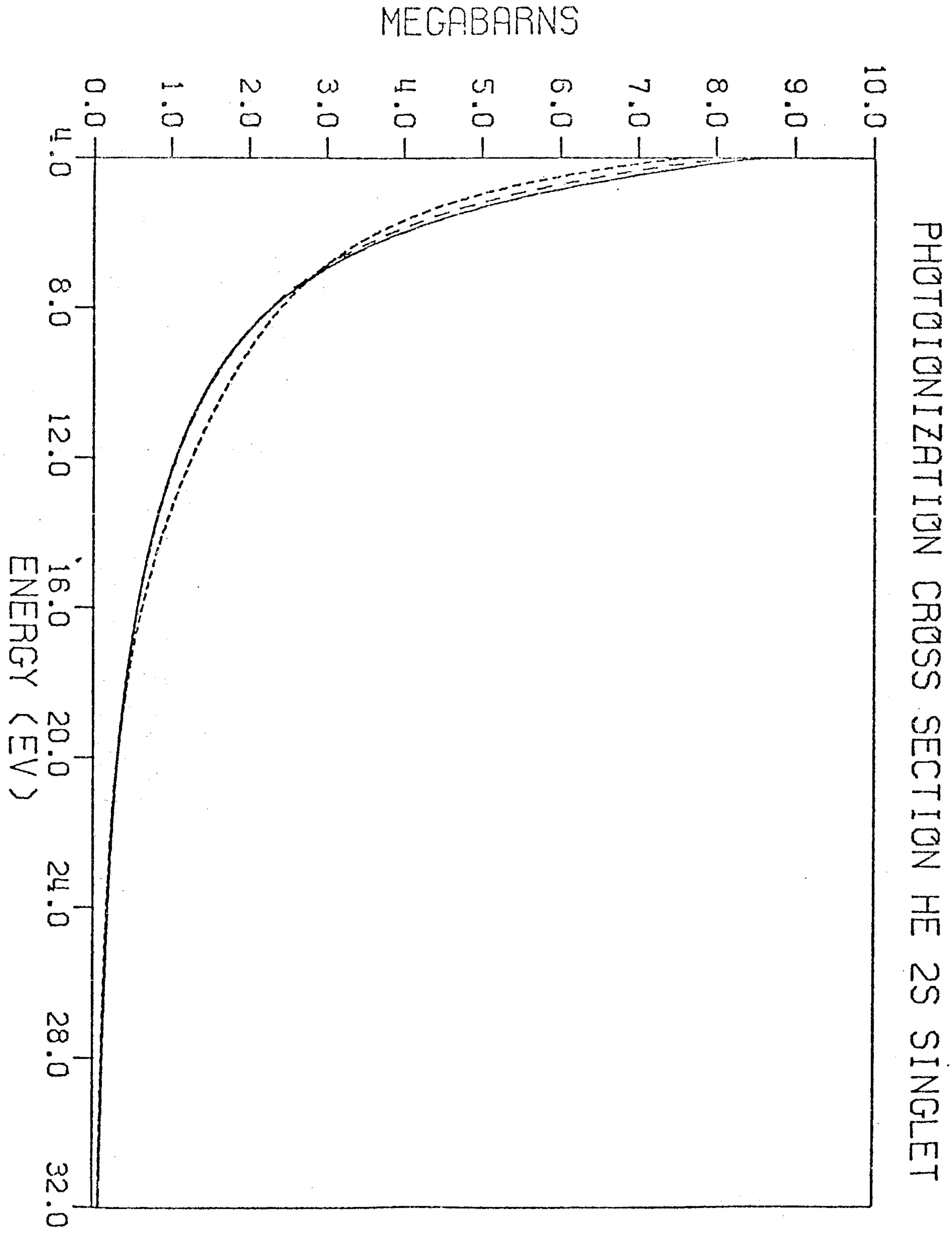

PHOTOIONIZATION CROSS SECTION HE 2S TRIPLET
MEGABARNS
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
4.7
8.7
12.7
16.7
20.7
24.7
28.7
32.7
36.7
40.7
ENERGY (EV)

Fig.II.6


PHOTOIONIZATION CROSS SECTION HE 2S SINGLET
MEGABARNS
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
ENERGY (EV)

calculations by Bell and Kingston[60] and by Duta, Duta and Das[61] agree well with the Geltman results and experiments. More recently, Langhoff[62] presented a calculation using his Stieltjes imaging approach. The results are presented in terms of "differential and cumulative oscillator-strength distributions." He claims that the results are correct. Now, using the oscillator strength distribution given in his paper, together with the expression that he gave for the Stieltjes imaging, we calculated the cross-sections. The values are in agreement with Geltman's results near the threshold and on the tail but not in the region of the maximum, where most of the experimental points are. So, it is not clear for us how to classify his results.

We performed two sets of calculations, one using a [10s/8p] and the other using a [10s/9p] basis set of contracted Gaussian type orbitals. The basis set specifications are shown in Tables II. 2 and II. 3 and the respective oscillator-strengths and transition frequencies in Tables II. 4 and II. 5. The resulting cross-sections for two different values of the parameter FAC in (II. 36), together with Geltman's results, are shown in Fig. II. 7 for the [10s/8p] basis set. We did not plot the results for the [10s/9p] basis set because the results do not differ appreciably. It is quite clear that we are very far from the correct results. Besides that, the analytical continuation shows a very poor convergence. We tried several choices of points in the complex plane without any improvement. So, if we insist on having confidence in the analytical continuation procedure, we have to attribute the failure of our results to the

Table II.2

H$^-$ (10s/8p) basis set specifications

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	H(-)	S	10.6072000	0.8333762
2	1	2	H(-)	S	38.6516300	0.1920389
3	1	3	H(-)	S	173.5822000	0.0350260
4	1	4	H(-)	S	1170.4980000	0.0042273
5	2	1	H(-)	S	3.3796490	1.0000000
6	3	1	H(-)	S	1.2025180	1.0000000
7	4	1	H(-)	S	0.4639250	1.0000000
8	5	1	H(-)	S	0.1905370	1.0000000
9	6	1	H(-)	S	0.0812406	1.0000000
10	7	1	H(-)	S	0.0285649	1.0000000
11	8	1	H(-)	S	0.0095210	1.0000000
12	9	1	H(-)	S	0.0031736	1.0000000
13	10	1	H(-)	S	0.0010578	1.0000000
14	11	1	H(-)	X	0.0056743	1.0000000
15	12	1	H(-)	X	0.0140543	1.0000000
16	13	1	H(-)	X	0.0170230	1.0000000
17	14	1	H(-)	X	0.0421630	1.0000000
18	15	1	H(-)	X	0.1119120	1.0000000
19	16	1	H(-)	X	0.3462700	1.0000000
20	17	1	H(-)	X	1.4583690	1.0000000
21	18	1	H(-)	X	5.0000000	1.0000000
22	19	1	H(-)	Y	0.0056743	1.0000000
23	20	1	H(-)	Y	0.0140543	1.0000000
24	21	1	H(-)	Y	0.0170230	1.0000000
25	22	1	H(-)	Y	0.0421630	1.0000000
26	23	1	H(-)	Y	0.1119120	1.0000000
27	24	1	H(-)	Y	0.3462700	1.0000000
28	25	1	H(-)	Y	1.4583690	1.0000000
29	26	1	H(-)	Y	5.0000000	1.0000000
30	27	1	H(-)	Z	0.0056743	1.0000000
31	28	1	H(-)	Z	0.0140543	1.0000000
32	29	1	H(-)	Z	0.0170230	1.0000000
33	30	1	H(-)	Z	0.0421630	1.0000000
34	31	1	H(-)	Z	0.1119120	1.0000000
35	32	1	H(-)	Z	0.3462700	1.0000000
36	33	1	H(-)	Z	1.4583690	1.0000000
37	34	1	H(-)	Z	5.0000000	1.0000000

Table II.3

H^- (10s/9p) basis set specifications

GAUSSIAN	FUNCTION	COMPONENT	CENTER	TYPE	EXPONENT	COEFFICIENT
1	1	1	H(-)	S	10.6072000	0.8223762
2	1	2	H(-)	S	38.6516300	0.1920389
3	1	3	H(-)	S	173.5822000	0.0350260
4	1	4	H(-)	S	1170.4980000	0.0042273
5	2	1	H(-)	S	3.3796490	1.0000000
6	3	1	H(-)	S	1.2025180	1.0000000
7	4	1	H(-)	S	0.4639250	1.0000000
8	5	1	H(-)	S	0.1905370	1.0000000
9	6	1	H(-)	S	0.0812406	1.0000000
10	7	1	H(-)	S	0.0285649	1.0000000
11	8	1	H(-)	S	0.0100400	1.0000000
12	9	1	H(-)	S	0.0035310	1.0000000
13	10	1	H(-)	S	0.0012420	1.0000000
14	11	1	H(-)	X	0.0011200	1.0000000
15	12	1	H(-)	X	0.0027750	1.0000000
16	13	1	H(-)	X	0.0068713	1.0000000
17	14	1	H(-)	X	0.0170230	1.0000000
18	15	1	H(-)	X	0.0421630	1.0000000
19	16	1	H(-)	X	0.1119120	1.0000000
20	17	1	H(-)	X	0.3462700	1.0000000
21	18	1	H(-)	X	1.4583690	1.0000000
22	19	1	H(-)	X	5.0000000	1.0000000
23	20	1	H(-)	Y	0.0011200	1.0000000
24	21	1	H(-)	Y	0.0027750	1.0000000
25	22	1	H(-)	Y	0.0068713	1.0000000
26	23	1	H(-)	Y	0.0170230	1.0000000
27	24	1	H(-)	Y	0.0421630	1.0000000
28	25	1	H(-)	Y	0.1119120	1.0000000
29	26	1	H(-)	Y	0.3462700	1.0000000
30	27	1	H(-)	Y	1.4583690	1.0000000
31	28	1	H(-)	Y	5.0000000	1.0000000
32	29	1	H(-)	Z	0.0011200	1.0000000
33	30	1	H(-)	Z	0.0027750	1.0000000
34	31	1	H(-)	Z	0.0068713	1.0000000
35	32	1	H(-)	Z	0.0170230	1.0000000
36	33	1	H(-)	Z	0.0421630	1.0000000
37	34	1	H(-)	Z	0.1119120	1.0000000
38	35	1	H(-)	Z	0.3462700	1.0000000
39	36	1	H(-)	Z	1.4583690	1.0000000
40	37	1	H(-)	Z	5.0000000	1.0000000

Table II.4

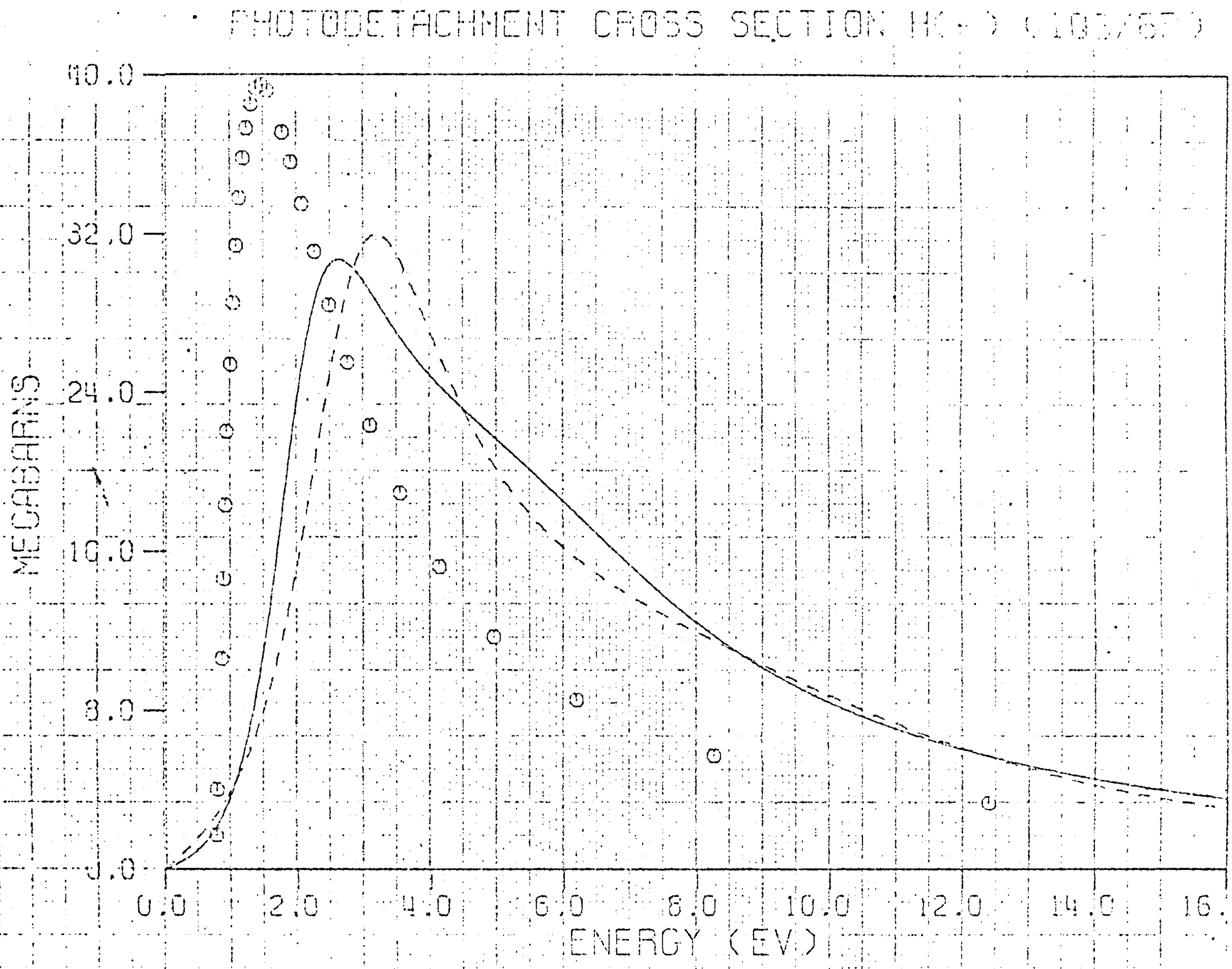
Oscillator Strengths and Transition frequencies for H(-), (10s/8p) basis set.

f	e(ev)
0.06272304	1.56257000
0.26558220	2.31630001
0.46963020	3.78369999
0.52111200	6.72270000
0.44172030	13.56780000
0.15872020	32.91817010
0.02170020	113.45640000
0.00363320	417.38163200

Table II.5

Oscillatros Strengths and Transition frequencies for H(-), (10s/9p) basis set.

f	e(eV)
0.00210	1.37270
0.02940	1.50200
0.15330	1.95600
0.44040	3.09870
0.67680	5.89450
0.50190	12.76760
0.16920	32.20540
0.02130	109.85530
0.00060	416.67750



PHOTODETACHMENT CROSS SECTION H(-) (103/67)
MEGABARNS
40.0
32.0
24.0
16.0
8.0
0.0
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
ENERGY (EV)

Fig.II.7

basis set. After all, somebody has to be guilty, the choice being done in a hierarchal manner, of course, But, at least in this case, the basis set, besides being the last member of the hierarchy, did a very bad job indeed. If we look to our distribution of transition frequencies, we see that the first pole occurs far away from the threshold (0.745 eV). And looking to the experimental results (better Geltman's results), we see that near the threshold the cross-section raises rapidly until a maximum value of 39.5 Mb (10^{-18} cm^2) at 1.45 eV. Since we do not have any poles at that region, we are not giving any information at all to the continued fraction in that region. That could be the main reason for the failure of the calculation. But to be really sure of that we need to perform a calculation with a larger basis set including more diffuse functions to get poles near the threshold.

We want now to make some comments about the method of analytical continuation and discuss some possible improvements.

4.4. Comments and Possible Improvements

There are a few things about the method, as it stands now, on which we would like to comment.

First of all there are some instabilities in the method which we still don't quite understand. For instance, in the 2^3S metastable state of helium it was necessary to remove one of the poles of the spectrum to obtain a good analytical continuation. The same was necessary for the H_2 case.[64] For the case of the hydrogen atom,[51] it was noted, without comments, that the best agreement was obtained if the bound-bound transitions were omitted from the spectrum. In our cases the type of instability noted was that for points near the omitted pole where the values of the cross sections suddenly changed sign. It has been suggested that what is needed to obtain a good analytical continuation is a smooth distribution of poles and oscillator-strengths. But now the problem is to define what is a smooth distribution. For instance, the distributions for H^- and H_2 given by Langhoff[48,62] appear to be smooth. We tried to analytically continue those distributions and the results are completely crazy. In this respect, note that the distributions for He 2^1S and 2^3S are not so smooth. It has something to do with the characteristics of the distribution, no doubt, but we don't know yet what exactly. It could be the smoothness of the spectrum, in the sense of having almost equally spaced poles carrying almost the same oscillator-strengths. It could be, but we are really afraid that what will come out when the whole story is solved is that "a smooth representation is that one which gives the right results." Some groups[65] are trying to refine the spectra, that is to obtain a new set of oscillator-strengths and transition frequencies from the ones found by some procedure, hoping that the new spectra would give a better analytical continuation. We don't know exactly what they are doing, but this could be done using the roots of the denominator of the Pade′ Approximant as the new poles. For the case of H^-, since we have only 9 poles, the best Pade′ which we could construct is a [4, 4] or maybe a [3, 5], which would give us a new spectra with only four or five poles. Since we don't know how many iterations would be necessary to get a smooth representation, if a second iteration should be necessary it would give us one or two poles. This is too little information to get a good analytical continuation. To test such a procedure we would need a large number of poles in the initial spectrum.

Another source of instability in the present method is the procedure that we used to fit the points in the complex plane. While the Schlessinger[40] algorithm provides a practical way of evaluating the coefficients of the continued fraction, the iterative nature of the process introduces serious instabilities. We observed several cases where, for very small differences in the parameter FAC, the coefficients of the continued fraction changed drastically, causing serious troubles for the convergence. Not only the evaluation of the coefficients are subject to instabilities, but also the evaluation of the continued fraction. Due to its application, the numerical stability in evaluating continued fractions is now being carefully investigated.[66]

We decided to investigate a possible improvement of the fitting procedure. Since a continued fraction is related to a Pade′ Approximant, we could evaluate the Pade′ instead of the continued fraction, avoiding this way the iterative procedure to calculate the coefficients of the continued fraction and its value. We want to form a Pade′ Approximant from a given set of values of the function at N points. In the Pade′ literature, this is called a Pade′ Approximant of type II. That is, we want a Pade′ to f(z), $f^{[M,L]}(z)$ such that:

$$f^{[M,L]}(z) \equiv \frac{P_M(z)}{P_L(z)} \equiv \frac{\sum_{i=0}^{M} p_i z^i}{\sum_{i=0}^{L} q_i z^i}$$

$$f^{[M,L]}(z_k) = f(z_k) \qquad k = 1, N$$

This is also called a N-point Pade′ Approximant, but, due to the confusion in the literature, we call it from now on a multipoint-unipiece Pade′ Approximant, indicating that the Pade′ is formed from N given points but with only one piece of information at that point, namely, the value of the function at that point. Now, instead of the recursive relation (II. 38), we have a set of linear equations that can be solved with highly accurate methods. For instance, in case we have the value of the function at five different points, we can form a [2, 2] Pade′ by equating:

$$\sum_{i=0}^{2} p_i z_j^i = f(z_j) \sum_{i=0}^{2} q_i z_j^i \qquad j = 1, 5$$

or putting $q_0 = 1$

$$\sum_{i=0}^{2} p_i z_j^i = f(z_j) \left[1 + \sum_{i=1}^{2} q_i z_j^i \right] \qquad j = 1, 5$$

Once the p's and q's are obtained, the evaluation of the Pade′ is straightforward. Its calculation will involve the evaluation of two polynomials and only one division. Since the system of linear equations can be solved accurately and since the same number of operations are involved in the evaluation of a continued fraction and a Padé of the same order, we expect that this scheme will represent an improvement on the fitting procedure. We have just set up a program[67] to do that, but we have not tested it yet. This will be just a test to verify how much improvement we can get avoiding the use of continued fractions. But we think that the best improvement will come from the procedure which we will describe below.

The basic assumption was that we could express the frequency dependent polarizability by

$$\alpha(\omega) = \sum_{n \neq 0} \frac{\tilde{f}_{on}}{\tilde{\omega}_{on}^2 - \omega^2}$$

The analytical form is correct. We are only assuming that the infinite series can be replaced by an "effective summation." But we are not making use at all of this analytical form. We are only using the expression to calculate $\alpha(z)$ at arbitrary points z. The analytical continuation may be improved if we give to the Padé, besides the value of the function at some points, some information about its analytical behavior. To accomplish this, we expand $\alpha(z)$ in a Taylor series around some arbitrary point z_0.

$$\alpha(z) = \alpha(z_0) + \frac{\partial \alpha}{\partial z}\Big|_{z_0} (z - z_0) + \cdots + \frac{1}{k!} \frac{\partial^k \alpha}{\partial z^k}\Big|_{z_0} (z - z_0)^k$$

Calculating the derivatives we get:

$$\alpha(z) = \sum \frac{\tilde{f}_{on}}{\tilde{\omega}_{on}^2 - z_0} + \left\{ \sum \frac{\tilde{f}_{on}}{(\tilde{\omega}_{on}^2 - z_0)^2} \right\} (z - z_0) + \cdots +$$

$$+ \left\{ \sum \frac{\tilde{f}_{on}}{(\tilde{\omega}_{on}^2 - z_0)^{k+1}} \right\} (z - z_0)^k$$

Now, given z_0 we can calculate the values of the coefficients of the Taylor series. Equating:

$$\alpha(z) = \alpha(z_0) + \sum_{k=1} \left\{ \sum_{n} \frac{\tilde{f}_{on}}{(\tilde{\omega}_{on}^2 - z_0)^{k+1}} \right\} (z - z_0)^k = \frac{P_M(z)}{Q_N(z)}$$

we get again a set of linear equations which can be solved for the coefficients of P_M and Q_N. With these coefficients the Pade′ Approximant can be evaluated. One possible argument against the procedure is the arbitrary choice of z_0. But the other procedure also involves the choice of arbitrary points and the same justification used for that can be used here. We set up a program to carry out this procedure and we chose helium as a test case.[68] Helium was chosen because almost everything works for helium despite its known inactiveness. We obtained some reasonable results for the cross-section up to ~60 eV where, for many choices of z_0, the cross-section started to raise again. Another observation was that at some choices of z_0, the cross-section exhibited jumps near some points. We decided to investigate if this behavior could be related to the zeros of $Q_N(z)$, but we found that the poles were far from those points. Consequently, we are led to conclude that the raisings at higher energies and the jumps for certain choices of z_0 were associated with the convergence of the Pade′. With this procedure, following the nomenclature that we adopted, we have a unipoint-multipiece Pade′ Approximant. So, although we now have information about the analytical behavior of the function, we have the value of the function at only one point. Maybe we are asking too much from the Pade′, since with information about one single point we want a description in a large range of energy values. The natural extension should be a multipoint-multipiece Pade′ Approximant.[69] That is a Pade′ formed from a given set of points where the value of the function and some of its derivatives are known. Now the problem can be very complicated. We have been talking about the necessity of having a certain number of poles to obtain a good representation. And now, with the conclusion above, the first thing that we could ask is how many points would be necessary to do that. In case a large number of points is necessary, this would imply the expansion in a Taylor series around all these points, equating these expansions to the Pade′ and solving a big number of linear equations involving the coefficients of the Pade′. But surprisingly enough, recent applications of multipoint-multipiece Pade′ Approximants showed that a two-point Pade′ Approximant can provide an accurate approximation to the expansion.[70, 71] So there is some hope that his procedure could be applicable in a practical way. We will try to see that.

REFERENCES

1. A. C. G. Mitchell and M. W. Zemansky, "Radiation and Excited Atoms", 2nd. edition, Cambridge University Press, 1961.
2. A. Dalgarno and A. E. Kinston, Proc. Phys. Soc., 73, 455 (1959).
3. S. Chandresahkar and D. Elbert, Ap. J., 128, 633 (1958).
4. R. W. Ditchburn and U. Opik, in "Atomic and Molecular Processes", ed. D. R. Bates, Academic Press, New York, 1962, p. 79.
5. L. M. Branscomb, ibid., p. 100.
6. A. L. Stewart in "Advances in Atomic and Molecular Physics", 3, 1 (1967).
7. G. V. Maar, "Photoionization Processes in Gases", Academic Press, New York, 1967.
8. L. G. Christophorou, "Atomic and Molecular Radiation Physics", Wiley-Interscience, London, 1971.
9. J. C. Slater, "Quantum Theory of Atomic Structure", Vol. I, McGraw-Hill Book Co., New York, p. 188.
10. See for instance P. Roman, "Advanced Quantum Mechanics", Addison-Wesley Publishing Co., New York, 1965, p. 160.
11. D. R. Bates, Month. N. Roy. Astron. Soc., 106, 432 (1946).
12. D. R. Bates, ibid., 100, 25 (1939).
13. D. R. Bates and H. S. W. Massey, Proc. Roy. Soc., A177, 329 (1941).
14. See for instance, J. C. Slater, "Quantum Theory of Atomic Structure", Vol. II, McGraw Hill Co. Inc., New York, 1960, p. 1.
15. V. Fock, Z. Physik, 61, 126 (1930).

16. M. J. Seaton, Phil. Trans. Roy. Soc. (London), A245, 469 (1953).
17. I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc., 53, 654 (1957); Trans. Roy. Soc. (London), A251, 113 (1958).
18. B. L. Moisiewitsch, "Variational Principles", Interscience Publishers, London, 1966, p. 274.
19. P. G. Burke in "Autoionization", ed. A. Temkin, Mono Book Co. Balt., 1966, p. 77.
20. K. Smith, "The Calculation of Atomic Collision Processes", Wiley-Interscience, New York, 1971, p. 194.
21. P. C. Burke and K. Smith, Rev. Mod. Phys., 34, 458 (1962).
22. P. G. Burke, Proc. Phys. Soc., 82, 443 (1963).
23. A. Tenkim, Phys. Rev., 107, 1004 (1957); ibid., 116, 358 (1959); ibid., 121, 788 (1961).
24. D. R. Bates, Proc. Roy. Soc. (London), 188, 350 (1947).
25. M. M. Klein and K. A. Bruekner, Phys. Rev., 111, 1114 (1958).
26. S. Geltman, Ap. J., 136, 935 (1962).
27. See for instance, ref. 10, p. 165.
28. M. J. Seaton, Month. N. Roy. Astron. Soc., 118, 504 (1958).
29. A. Burges and M. J. Seaton, ibid., 120, 121 (1960).
30. See for instance, N. F. Mott and H. S. W. Massey, "The Theory of Atomic Collisions", 3rd. edition, Oxford Press, London, 1965, p. 43.
31. M. J. Seaton, Proc. Phys. Soc., 88, 815 (1966).
32. U. Fano and J. W. Cooper, Rev. Mod. Phys., 40, 441 (1968).
33. M. Y. Amusya, N. A. Cherepkov, L. V. Chernoysheva, Soviet Physics JETP, 33, 1 (1971); Phys. Letters, 40A, 5 (1972).

34. M. Schwartz, "Principles of Electrodynamics", McGraw Hill Book Co., New York, 1972, p. 300.

35. See for instance ref. 10, pp. 174, 198, 337.

36. See ref. 34, p. 256.

37. See for instance, W. T. Scott, "The Physics of Electricity and Magnetism", John Wiley Inc., New York, 1962, p. 516.

38. See for instance, P. W. Atkins, "Molecular Quantum Mechanics", Clarendon Press, 1970, p. 409.

39. A. Dalgarno and N. Lynn, Proc. Phys. Soc., 70, 802 (1957).

40. R. W. Haymaker and L. Schlessinger in, "The Pade Approximant in Theoretical Physics", eds. G. A. Baker and L. Gammel, Academic Press, New York, 1970, p. 257.

41. H. Pade, Ann. Ecole Normale Superieure, Paris, 9 (1892); 16 (1899).

42. G. A. Baker, Adv. Theoret. Phys., 1, 1 (1965).

43. P. R. Graves-Morris, editor, "Pade Approximant and their Application", Academic Press, New York, 1972.

44. G. A. Baker and J. L. Gammel, editors, "The Pade Approximant in Theoretical Physics, Academic Press, New York, 1970.

45. J. L. Basdevant, Fort. Phys., 20, 283 (1972).

46. G. A. Baker, "Essentials of Pade Approximant", Academic Press, New York, 1975.

47. H. S. Wall, "The analytic Theory of Continued Fractions", Van Nostrand, New Jersey, 1948.

48. P. W. Langhoff and M. Karplus, J. Opt. Soc. Amer., 59, 863 (1969); J. Chem. Phys., 52, 1435 (1970).

49. P. H. S. Martin, T. N. Resigno, V. McKoy and W. H. Henneker, Chem. Phys. Letters, 29, 496 (1974).

50. T. N. Resigno, C. W. McCurdy and V. McKoy, Phys. Rev., 9, 2409 (1974).

51. J. Broad and W. P. Reinhardt, J. Chem. Phys., 60, 2182 (1974).

52. D. L. Yeager, M. A. C. Nascimento and V. McKoy, Phys. Rev. A., accepted for publication.

53. V. Jacobs, Phys. Rev. A, 3, 289 (1971); A. Dalgarno, H. Doyle and M. Oppenheimer, Phys. Rev. Letters, 29, 1051 (1972); S. S. Huang, Ap. J. 108, 354 (1948).

54. D. W. Norcross, J. Phys. B., 4, 652 (1971).

55. V. L. Jacobs, Phys. Rev. A, 9, 1938 (1974).

56. R. F. Stebbings, F. B. Dunning, F. K. Tittel and R. D. Rundell, Phys. Rev. Letters, 30, 815 (1973).

57. S. Chandrasekhar, Ap. J., 128, 114 (1958) and references therein.

58. T. L. John, Month. N. Roy. Astron. Soc., 121, 41 (1960).

59. S. J. Smith and D. S. Burch, Phys. Rev., 116, 1125 (1959).

60. K. L. Bell and A. E. Kingston, Proc. Phys. Soc., 90, 895 (1967).

61. N. C. Dutta, C. M. Dutta and T. P. Das, Phys. Rev. A, 2, 2289 (1970).

62. P. W. Langhoff and C. T. Corcoran, J. Chem. Phys., 61, 146 (1974).

64. P. H. S. Martin, private communication.

65. V. McKoy, personal communication.

66. W. B. Jones and W. J. Thorn, Mathematics of Computation, 28, 795 (1974) and references therein.

67. P. H. S. Martin and M. A. C. Nascimento, work in progress.

68. M. A. C. Nascimento and P. H. S. Martin, unpublished results.

69. M. Bransley, J. Nath. Phys., 14, 299 (1973).

70. P. Sheng and J. D. Down, Phys. Rev. B, 4, 1343 (1971).

71. A. Isihara and E. W. Montroll, Proc. Nat. Acad. Sci. USA, 68, 3111 (1971).

Section III

Experimental determination of the cross-sections

It is not our intention to give a complete account of the experimental techniques used to determine the photoionization cross-sections. This section was included to give a general idea of the techniques and the main difficulties involved in the measuring process. For the details the reader is referred to the literature cited along the discussion as well as the reviews by Samson,[1] McDaniell,[2] Branscomb,[3] and Mann.[4] We will discuss mainly the techniques for photodetachment cross-sections, where the production of the ions in a workable concentration poses a special problem over the photoionization of neutral species. The importance of knowing photodetachment cross-sections for several negative species has been discussed in the introductory section (Part I). Since one of the main problems for the measurement is the production of a workable ion-current, this fact per se amply justifies the theoretical calculation of the cross-sections. Even in the cases where a workable ion-current is obtained, the measurements are subject to several other sources of errors and, again, theoretical results are important to clarify the situation. On the other hand, if a very accurate measurement is possible, that will help in deciding the quality of the calculations.

1. Crossed-Beam Method

This is a general method that can be used to measure cross-sections of almost all scattering processes. It has been used to study elastic and inelastic collisions of electrons with atoms and molecules, including metastable states and ionized atoms. But, in fact, the first use of this technique was made in the study of photodetachment of $H^{\ominus}$ ions by Branscomb and Fite.[1] In this first experiment the photodetachment was observed but no measurement of the cross-section was possible. One year later Branscomb and Smith[5] succeeded in measuring absolute cross-sections for $H^{\ominus}$ detachment. The apparatus was further improved and in 1959 Smith and Burch[6] did a careful relative measurement of the cross-section for $H^{\ominus}$ in a range of 4000Å to 13,000 Å.

Basically, the technique consists of crossing a beam of photons of known wavelength at right angle with a beam of ions ($H^{\ominus}$) with known velocity. The detached electrons are collected and detected. Let's see how many problems are involved in the measurement process. Let's divide the problem in three separate parts: a) photon beam, b) ion beam and c) detection of the electrons.

The photon beam must be a stable source of light, of well known spectral distribution. Now, since the cross-section is to be measured as a function of the wavelength, and since the source is obviously not monochromatic, filters have to be used to select the wavelength. This introduces a new problem, that of the bandwidth versus transmittance of the filters, and the dependence on the wavelength. After the filtering and focusing the beam intensity must be measured by means of a radiometer, which introduces another source of error. In the earlier experiments, a projection lamp of tungsten filament was used, being later replaced by a brighter but less stable carbon arc projection lamp. This instability forced the development of a method for monitoring the light beam.

The ion beam if produced by electrical discharge in the vapor which can produce the desired ion. In case of H^- it was found that the mixture of $D_2O + H_2$ was more effective in producing H^- and D^- ions. The ions are separated by means of a 90° sector magnetic field. The velocity of the ion has to be known and besides that it has to be focused.

Finally in the reaction chamber, the ejected electrons have to be all collected and a small current has to be measured. The ejected electrons are collected by double-focusing electric and magnetic fields. Electron currents generated are of the order of 10^{-12} amp.

Now, consider a $H^{\ominus}$ ion moving in the x direction with a velocity v. At a point x it is illuminated with a normally incident radiant flux, $\phi(x,\lambda)\,d\lambda$, of light in the wavelength range λ to $\lambda + d\lambda$. The probability that the ion will lose an electron in the path interval dx is

$$P dx = \frac{dx}{vhc} \int \sigma(\lambda)\,\phi(x,\lambda)\,\lambda\,d\lambda \quad .$$

Define $\phi'(\lambda)$ as the normalized radiant flux such that

$$\phi(x,\lambda) = \phi'(\lambda)\,\frac{\omega(x)}{s}$$

where s is a distance, perpendicular to the ion beam, over which the light intensity is reasonably constant, and $\omega(x)/s$ is the power density at the ion beam. Then the probability of detachment when an ion passes a distance L through the ion beam is:

$$P = \frac{1}{hcvs} \int_\lambda \sigma(\lambda)\, \phi'(\lambda)\, \lambda \int_x \omega(x)\, dx\, d\lambda$$

$$= \frac{\overline{W}}{hcvs} \int_\lambda \sigma(\lambda)\, \phi'(\lambda)\, \lambda\, d\lambda \qquad \text{(III.1)}$$

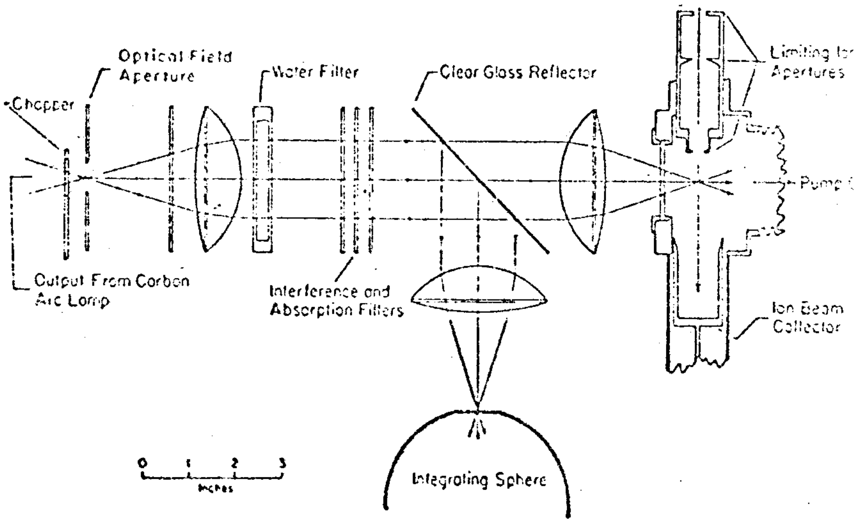
where $\overline{W} = \int_0^L \omega(x)\, dx$ is the average total power incident on the area sL. Now, if j_i is the ion current and j_e is the electron current in the illuminated region,

$$P_{exp} = j_e/j_i \qquad \text{and}$$

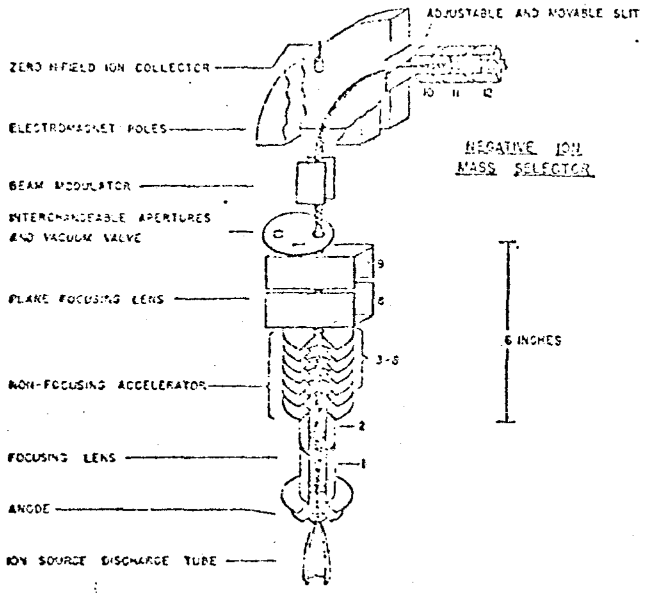
$$\frac{j_e}{j_i} = \frac{\overline{W}}{hcvs} \int \sigma(\lambda)\, \phi'(\lambda)\, \lambda\, d\lambda\ .$$

Then, a measurement of j_e and j_i gives the experimental probability of detachment per ion. If the spectral density of the light source $\phi'(\lambda)$ and the quantities $\overline{W}$, s, v are measured, $P_{theo.}$ can be calculated from (III.1) inserting theoretical values of σ. In the 1955 measurement of Branscomb and Smith,[5] P_{exp} was determined with 10-13% of error, the main errors coming from the measurement of $\overline{W}$, electron current and radiometer height. When compared with the $P_{theo.}$ obtained from the

Fig. III.1



Schematic diagram showing the arrangement of the optical system in relation to the ion beam. Light intensity in the integrating sphere is monitored with a bolometer.



The arrangement of ion optical elements in the high transmission low resolution mass selector is shown. Functions of the various elements are discussed in the text.

Fig.III.2a

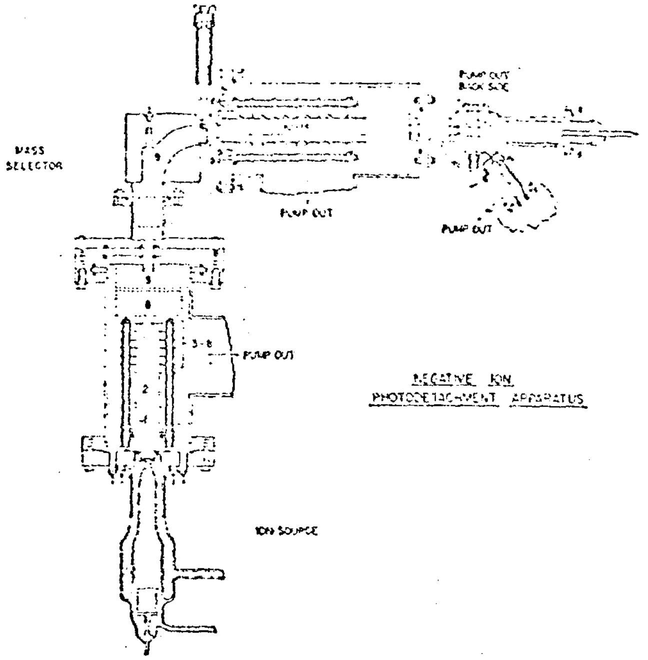


Diagram of the negative ion beam apparatus used for photodetachment measurements. The dashed rectangle in the reaction chamber indicates the position, shape, and relative size of the photon beam at the intersection with the ion beam.

Fig. III.2b

available calculations, the conclusion was that all the calculations were in the range of the experimental error. While the experiment showed a great effort to develop experimental methods to measure cross-sections, it didn't clarify the theoretical situation, since the shape of the curves for $\sigma(H^-)$ at that time varied from calculation to calculation, but in the light of the experiment all were equally correct.

Because of the difficulties involved in radiometric calibrations and in proving that all photodetached electrons are collected, absolute cross-sections are much more difficult to obtain than relative ones. Besides that, in the 1955 experiment, the fact that monochromatic light of sufficient intensity was not available forced the measurements of integrated cross-sections over a wide spectral range.

A relative measurement of $\sigma(H^-)$ was made in 1959 by Smith and Burch.[6] The apparatus is shown in Figures 1 and 2, and is fully described in the references.[6,7]

To counterbalance the use of narrow band filters, the source of light had to be much more intense, and the tungsten filament lamp was replaced by a carbon arc lamp.

In terms of the transmission of the optical system equation (III.1) can be rewritten:

$$j_e = k j_i W \int \sigma(\lambda) T(\lambda) \phi(x) \left(\frac{\lambda}{hc}\right) d\lambda \qquad \text{(III.2)}$$

where $T(\lambda)$ is the transmission of the optical system, k contains geometrical factor and the ion beam velocity and the other quantities are the same defined above.

Assuming that the cross-section varies linearly within the band

$$\sigma(\lambda) = \sigma_0 + \sigma_1 \lambda$$

we have

$$P = \frac{j_e}{j_i} = kW \left[\sigma_0 \int \phi(\lambda)\, T(\lambda)\, \lambda d\lambda + \sigma_1 \int \phi(\lambda)\, T(\lambda)\, \lambda^2 d\lambda\right] \qquad \text{(III. 3)}$$

Defining

$$\lambda_2 = \int \phi(\lambda)\, T(\lambda)\, \lambda^2 d\lambda \Big/ \int \phi(\lambda)\, T(\lambda)\, \lambda . d\lambda$$

and

$$\lambda_1 = \int \phi(\lambda)\, T(\lambda)\, \lambda\, d\lambda \Big/ \int \phi(\lambda)\, T(\lambda)\, d\lambda ,$$

equation (III. 3) can be written:

$$P = \frac{j_e}{j_i} = kW\sigma(\lambda_2)\, \lambda_1 \int \phi(\lambda)\, T(\lambda)\, d\lambda .$$

By identifying individual bandpass filters with a subscript m, we can write

$$\sigma(\lambda_{m2}) = P_m / kW\lambda_{1m} \int \phi(\lambda)\, T_m(\lambda)\, d\lambda$$

$$= (j_e)_m / j_i k \lambda_{m1} W_m \qquad \text{(III. 4)}$$

For the filters used in the work by Smith and Burch no significant error was introduced by assuming $\lambda_{m2} = \lambda_{m1}$.

Then we can finally write:

$$\sigma(\lambda_m) = (j_e)_m / j_i k \lambda_m W_m \quad . \qquad \text{(III.5)}$$

The value of the cross-section for the filter $m = 7$ ($\lambda = 5280$ Å) wasd etermined and the other measurements were made relative to this wavelength. The estimated error in the measurement is about 2%. Now, these relative measurements can be put in absolute scale with 10% of error, using the earlier values of absolute cross-sections. When that was done, the results showed that all calculations presented a discrepancy of 20% in the values of σ across the spectral range of 4000 Å to 13,000 Å. This result reactivated the theoretical calculations of $\sigma(H^-)$, as discussed in the last section.

This method has been also used with the photo-detachment cross-section of O^-, C^-, S^-, I^-, OH^-, SH^-.[8]

2. Other Methods

It is possible by means of shock-wave heating to produce an atmosphere of negative halogen atomic ions with concentrations of the order 10^{15} cm^3, over a region with lateral dimensions of order 10 cm. As photodetachment cross-sections are of the order of 10^{-17} cm^2, absorption of light by negative ions should be observable photographically. With this technique, photodetachment absorption spectra have been observed for F^-, Cl^-, Br^- and I^-.[9]

Tunable laser light sources, with their inherent advantages of higher photon flux and narrow bandwidth, and particularly dye lasers in the range 3500 - 7000 Å, are now being used to make a major improvement in photodetachment studies. The use of these sources in photodetachment studies was initiated by Lineberger. Several measurements have been done by now, namely photodetachment of S^-, OH^-, OD^-, NO_2^- and alkali-atoms electron-affinities.[10]

More recently the use of ion cyclotron techniques was introduced in the study of photodetachment processes. These techniques made a great improvement in the production of the ion beams, since the ion cyclotron spectrometer can be used to generate, trap and detect the negative ions. Since in these systems the ions can be trapped efficiently for long periods of time, high negative ion densities are not needed, and a wide variety of ions can be studied. These techniques were introduced by Brauman and co-workers, and have been apllied to the photodetachment of several species like PH_2^-,[11] NO_2^-,[12] OH^-,[13] NH_2^- and AsH_2^-.[14]

With the rapid development in the lasers technology it is probable that in the near future, tunable lasers in a wide region of the spectrum will be available, solving at least the problem of light source.

References

1. J. A. Samson, Adv. Atomic Mol. Phys. 2, 178 (1966).
2. E. W. McDaniel in "Collision Phenomena in Ionized Gases", John Wiley, New York, 1964, p. 338.
3. L. M. Branscomb in "Atomic and Molecular Processes", ed. D. R. Bates, Academic Press, New York, 1962, p. 100.
4. G. V. Maar, "Photoionization Processes in Gases", Academic Press, New York 1967.
5. L. M. Branscomb and W. L. Fite, Phys. Rev. 93, 651(A) (1954); L. M. Branscomb and S. J. Smith, ibid., 98, 1028 (1955).
6. S. J. Smith and D. S. Burch, Phys. Rev., 116, 1125 (1959).
7. S. J. Smith and L. M. Branscomb, Rev. Sci. Instrum. 31, 733 (1960).
8. M. L. Seman and L. M. Branscomb, Phys. Rev. 125, 1602 (1962); L. M. Branscomb, D. S. Burch, S. J. Smith and S. Geltman, ibid. 111, 504 (1958); L. M. Branscomb and S. J. Smith, J. Chem. Phys. 25, 598 (1956); L. M. Branscomb, Phys. Rev. 148, 11 (1966); B. Steiner, J. Chem. Phys. 49, 5097 (1968).
9. R. S. Berry, C. W. Reimann and G. N. Spokes, J. Chem. Phys. 35, 2237 (1961); 37, 2278 (1962); R. S. Berry and C. W. Reimann, ibid. 38, 1540 (1963).
10. W. C. Lineberger and B. W. Woodward, Phys. Rev. Letters, 25, 424 (1970); H. Hotop, T. A. Patterson and W. C. Lineberger, J. Chem. Phys. 60, 1806 (1974); E. Herbst, T. A. Patterson and W. C. Lineberger, ibid. 61, 1300 (1974).
11. K. C. Smith and J. I. Brauman, J. Chem. Phys. 56, 1132 (1972).

References (continued)

12. J. H. Richardson, L. M. Stephenson, and J. I. Brauman, Chem. Phys. Letters 25, 318 (1974).

13. K. C. Smith and J. I. Brauman, J. Amer. Chem. Soc. 91, 7778 (1969).

14. K. C. Smith and J. I. Brauman, J. Chem. Phys. 56, 4626 (1972).

Section IV

The Random Phase Approximation

1. Philosophy of the EOM Method[1]

The main problem in quantum mechanics is the calculation of the wave function for a given system from which all the information about the system can be extracted. This is implied in the solution of the Schroedinger equation for the given system, but, since it can be exactly solved only for H and He^+, we have to use approximate methods for dealing with larger systems of chemical interest. Several ab-initio as well as semi-empirical procedures have been developed for this purpose.[2, 3] Sometimes we are interested not in a specific property of a certain state of the system but in something involving two different states of the system, for instance transition energies and transition moments. To obtain those, information via wave-function will have to be calculated for both states involved to extract the information. The best way possible to get accurate enough wave functions involves the use of extensive configuration interaction procedures.

Now, suppose that instead of trying to obtain accurate wave functions, we decide to concentrate efforts in obtaining relative properties between the states, namely, the energy of the excited-states relative to the ground state and the respective transition moments. It is possible to develop such an approach, where equations are set up to calculate directly those observable properties without worrying about total wave functions.

This is the philosophy behind the Equations of Motion Method, that is to obtain the best possible values for the observables without trying to get accurate wave functions.

Besides being a realistic approach, the EOM method presents important properties. First of all, it is a rigorous exact equation and to solve it exactly would correspond to exactly solving the Schroedinger equation for the system. Since this is impossible, approximate schemes for the EOM have been proposed, the RPA[4] being its lowest order approximation. In addition, the sum-rules for oscillator and rotational strengths are satisfied in this approach.[5] Another interesting property is that the length and velocity forms of the oscillator-strengths are identical in the RPA approximation.[6] This is a very useful property, since it can be used as a check for the basis set used to set up the equations. We proceed now with a brief discussion of the method.

2. The Equation of Motion[1]

The basic idea is to find an operator $0_\lambda^\dagger$ which, acting on the ground state of the system $|0\rangle$, generates an excited state $|\lambda\rangle$ and solves the equation of motion for its amplitudes. So by definition:

$$0_\lambda^\dagger |0\rangle = |\lambda\rangle \qquad \text{(IV. 1)}$$

Similarly, one can define 0_λ such that:

$$0_\lambda |0\rangle = 0 \qquad \text{(IV. 2)}$$

Then, for any hamiltonian H and the operators defined above, the following relations hold:

$$[H, 0_\lambda^\dagger]|0\rangle = (E_\lambda - E_0)\, 0_\lambda^\dagger|0\rangle = \hbar\omega_\lambda\, 0_\lambda^\dagger|0$$

$$[H, 0_\lambda]|0\rangle = -\hbar\omega_\lambda\, 0_\lambda|0\rangle = 0 \qquad \text{(IV. 3)}$$

So, if the form of the operator $0_\lambda^\dagger$ was known, we could calculate the transition frequencies. Unfortunately, in general it is not possible to find an operator $0_\lambda^\dagger$ such that its commutator with the Hamiltonian is proportional to it, the constant of proportionality being the transition frequencies, when applied to a given state. So, we have to try an approximate form for $0_\lambda^\dagger$. Before doing that, let's put equations (IV. 3) in another form. First, premultiply the first by $\delta 0_\lambda$, a variation in 0_λ, and the second by $\delta 0_\lambda^\dagger$ and close both with the ground state to get:

$$\langle 0|\delta 0_\lambda [H, 0_\lambda^\dagger]|0\rangle = \hbar\omega_\lambda \langle 0|\delta 0_\lambda\, 0_\lambda^\dagger|0\rangle$$

$$\langle 0|\delta 0_\lambda^\dagger [H, 0_\lambda]|0\rangle = -\hbar\omega_\lambda \langle 0|\delta 0_\lambda^\dagger 0_\lambda|0\rangle \qquad \text{(IV. 4)}$$

Now, take the difference between one equation and the hermitian conjugate of the other to get:

$$\langle 0|\{\delta 0_\lambda, [H, 0_\lambda^\dagger]\}|0\rangle = \hbar\omega_\lambda \langle 0|\{\delta 0_\lambda, 0_\lambda^\dagger\}|0\rangle$$

$$\langle 0|\{\delta 0_\lambda^\dagger, [H, 0_\lambda]\}|0\rangle = -\hbar\omega_\lambda \langle 0|\{\delta 0_\lambda^\dagger, 0_\lambda\}|0\rangle \qquad \text{(IV. 5)}$$

Instead of (IV. 5) the equations of motion are usually written in a more symmetrical form. Introducing the definition of the double commutator:

$$2[\delta O_\lambda, H, O_\lambda^\dagger] = [\delta O_\lambda, [H, O_\lambda^\dagger]] + [[\delta O_\lambda, H], O_\lambda^\dagger]$$

we can write (IV. 5) as

$$\langle 0|[\delta O_\lambda, H, O_\lambda^\dagger]|0\rangle = \hbar\omega_k \langle 0|[\delta O_\lambda, O_\lambda^\dagger,]|0\rangle \qquad \text{(IV. 6)}$$

Equations (IV. 5a) and (IV. 6) are identical only when $|0\rangle$ is the true ground state, since in this case:

$$\langle 0|[[O_\lambda^\dagger, \delta O_\lambda], H]|0\rangle = i\hbar \frac{d}{dt} \langle 0|[O_\lambda^\dagger, \delta O_\lambda]|0 = 0$$

This last remark is important because in general we have to accept some approximation for the true ground state $|0\rangle$, in which case the result above may not hold.

Calling $|\phi\rangle$ the approximate ground state, we finally get:

$$\langle \phi[\delta O_\lambda, H, O_\lambda^\dagger]|\phi\rangle = \hbar\omega \langle \phi[\delta O_\lambda, O_\lambda^\dagger]|\phi\rangle \qquad \text{(IV. 7)}$$

which is the equation of motion we try to solve. The only approximation made up to now was to take $|\phi\rangle$ as the true ground state.

3. Solutions to the Equations of Motion. The RPA Approximation

Before discussing the solution of the equation of motion we will introduce briefly some concepts of second quantization, since that is the common language in many-body theory. For an introductory but very clear discussion of second quantization the reader is referred to the books by Mattuck,[7] Landau[8] and Raimes.[9] A full coverage of the subject is given in a book by Berezin.[10]

In the second quantization formalism, instead of specifying a system by giving the spatial and spin coordinates of all its constituents, it is specified by giving the occupation number of each of its levels. Then, given a system and basis set, it will be specified by giving the occupation number of each single particle state. The system is then described by a set of numbers, the occupation numbers, and can be represented as:

$$\Psi = |n_1, n_2, n_3, \ldots, n_N\rangle$$

where $n_1, n_2, \ldots$ etc. are the occupation numbers for levels 1, 2, ... etc. For fermions, following the Pauli exclusion principle, the occupation numbers may assume only the values 1 or 0. For a given system in the ground-state, the highest filled single-particle state is called the Fermi-level. The various excited states can be formed by removing a particle from a state below the Fermi-level and placing it in a state above the Fermi-level. The picture can be further simplified if, referring to the ground state, we keep track only of the particles being transferred and the empty states left behind, in the formation of the excited states. The empty states are called "holes" and the single-particle states above the Fermi-level are called particles. This simplified description is called the "particle-hole" description.

To form the excited state from a given ground state, "creation" and "annihilation" operators are defined in the following way:

$$c_i^\dagger |n_1, n_2, \ldots, n_i, \ldots, n_N\rangle = (1-n_i)(-1)^{\Sigma_i} |n_1, n_2, \ldots, n_i+1, \ldots, n_n\rangle$$

$$c_i |n_1, n_2, \ldots, n_i, \ldots n_N\rangle = n_i(-1)^{\Sigma_i} |n_1, n_2, \ldots, n_i-1, \ldots, n_n\rangle$$

These definitions apply to fermions; there are equivalent definitions for bosons. We will be dealing only with fermions and all properties related to these operators will be valid for fermions. In the definitions above we have:

$$(-1)^{\Sigma_i} = (-1)^{\Sigma(n_1+n_2+,\ldots, n_{i-1})}$$

An excitation out of the ground state can be described by the successive application of these operators. For instance:

$$c_3 c_5^\dagger |1\ 1\ 1\ 0\ 0\ \ldots\rangle = |1\ 1\ 0\ 0\ 1\ \ldots\rangle$$

The following properties involving these operators can be derived by applying them to a given state and following the definitions:

$$[c_\ell c_k^\dagger]_+ = \delta_{\ell k}, [c_\ell, c_k]_+ = [c_\ell^\dagger, c_k^\dagger]_+ = 0$$

with the sign + indicating the anticommutator. To express the usual quantum operators in terms of creation and annihilation operators, we just require equality between the matrix elements of the operator in both formalisms. For instance, for a one-body operator, 0, we can write:

$$0_{ij} = \langle \phi_i | 0 | \phi_j \rangle = \int \phi_i^* 0 \phi_j dv$$

This operator can be expressed in second quantization formalism by:

$$0^s = \sum_{k,\ell} 0_{k\ell} c_k^\dagger c_\ell ,$$

which can be checked by taking the matrix element:

$$\langle 0\ 0 \ldots 1_i\ 0 \ldots | 0^s | 0\ 0 \ldots 1_j \ldots \rangle = \sum_{k,\ell} 0_{k\ell} \langle 0\ 0 \ldots 1 \ldots | c_k^\dagger c_\ell | 0\ 0 \ldots 1_j \ldots \rangle =$$

$$= \sum_{k,\ell} 0_{k\ell}\, \delta_{\ell j}\, \delta_{ik} = 0_{ij}$$

Similarly, it can be shown that any two-body operator becomes[9]

$$0^s = \sum_{k\ell mn} 0_{k\ell mn} c_\ell^\dagger c_k^\dagger c_m c_n$$

where

$$0_{k\ell mn} = \int \phi_k^*(1)\, \phi_\ell^*(2) 0\ \phi_m(1) \phi_n(2)\, dv_1\, dv_2$$

Just one more definition and we will be back to the equations of motion. Now, to avoid confusion let us label the particle states with letters m, n, p, q and hole states γ, δ, μ, ν. Then let us define a particle-hole pair creation and annihilation operator by the relations:

$$C^{\dagger}(m\gamma) = c^{\dagger}_{m} c_{\gamma}$$

$$C(m\gamma) = c^{\dagger}_{\gamma} c_{m}$$

Now, in the RPA approximation to the equations of motion, the ground state $|0\rangle$ is taken as the Hartree-Fock ground state $|HF\rangle$. But, since it is admitted that the true ground state is not simply $|HF\rangle$, the form of the operator $0^{\dagger}_{\lambda}$ should express the possibility of the $|\lambda\rangle$ state being formed by excitation from the $|HF\rangle$ ground state as well as from "de-excitations" from the true correlated ground state. In other words, particle-hole creation as well as annihilation operators should be included in $0^{\dagger}_{\lambda}$. In the RPA approximation, only single excitations are considered and the operator is written:[11]

$$0^{\dagger}(\lambda SM) = \sum_{m\gamma} \left\{ Y_{m\gamma}(\lambda S)\, C^{\dagger}_{m\gamma}(SM) - Z_{m\gamma}(\lambda S)\, C_{m\gamma}(\overline{S}\,\overline{M}) \right\} \qquad \text{(IV. 8)}$$

where Y and Z are the amplitudes for the excitation and "de-excitation" processes, and $C^{\dagger}_{m\gamma}(SM)$ is now a spin adapted particle-hole pair creation operator defined:[11]

$$C^{\dagger}_{m\gamma}(0\ 0) = (1/\sqrt{2})\left\{ c^{\dagger}_{m\alpha} c_{\gamma\alpha} + c^{\dagger}_{m\beta} c_{\gamma\beta} \right\}$$

$$C^{\dagger}_{m\gamma}(1\,M) = -c^{\dagger}_{m\alpha} c_{\gamma\beta} \qquad M = +1$$

$$= (1/\sqrt{2})(c^{\dagger}_{m\alpha} c_{\gamma\alpha} - c^{\dagger}_{m\beta} c_{\gamma\beta}) \qquad M = 0$$

$$= c^{\dagger}_{m\beta} c_{\gamma\alpha} \qquad M = -1$$

where α and β denote spin states. In (IV. 8)

$$C_{m\gamma}(\overline{S}\,\overline{M}) = (-1)^{S+M}\, C_{m\gamma}(S - M)$$

Now, substituting (IV. 8) in (IV. 7) and using the Hartree-Fock wave function, the equation for the amplitudes Y and Z in the RPA approximation is obtained and can be written in a matrix form as as:[11]

$$\begin{bmatrix} A^{\circ}(S) & B^{\circ}(S) \\ -B^{\circ *}(S) & -A^{\circ *}(S) \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = (\lambda S) \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} \qquad \text{(IV. 9)}$$

where the elements of the A and B matrices are given by:[11]

$$\begin{aligned} A^{\circ}_{m\gamma,\, n\delta}(S) &= \langle HF |\, [C_{m\gamma}(SM),\, H,\, C^{\dagger}_{n\delta}(SM)] \,| HF \rangle \\ &= \delta_{mn}\,\delta_{\gamma\delta}\,(\epsilon_m - \epsilon_\gamma) - V_{m\delta n\gamma} + \delta_{S,\,0}(2\,V_{m\delta\gamma n}) \end{aligned}$$

$$\text{(IV. 10)}$$

$$\begin{aligned} B^{\circ}_{m\gamma,\, n\delta}(S) &= -\langle HF |\, [C_{m\gamma}(SM),\, H,\, C_{n\delta}(\overline{S}\,\overline{M})] \,| HF \rangle \\ &= -(-1)^{S}\, V_{mn\delta\gamma} + \delta_{S,\,0}\,(2\,V_{mn\gamma\delta}) \end{aligned}$$

In equations (IV. 10), ϵ_i are the HF orbital energies and $V_{ij\ell k}$ are the usual two-electron integrals. Then, given a $|HF\rangle$ the matrices A and B are set up and (IV. 9) is solved for the amplitudes $Y(\lambda S)$ and $Z(\lambda S)$ and $\omega(\lambda S)$. These amplitudes are elements of the transition density matrix $\rho_{o\lambda}$, which can be used to determine matrix elements of any one-particle operator.[12] In our case we are interested in the dipole matrix elements.

Now, we are interested in determining the transition moments between two excited states, λ_i and λ_j, $\langle \lambda_i | M | \lambda_j \rangle$, when $\langle 0 | M | \lambda_i \rangle$ and $\langle 0 | M | \lambda_j \rangle$ are known.

Since this information is contained in Y and Z, one expression relating $\langle \lambda_i | M | \lambda_j \rangle$ and $Y(\lambda_i)$, $Y(\lambda_j)$, $Z(\lambda_i)$ and $Z(\lambda_j)$ will do the job. From the definition of the operator $0_\lambda^\dagger$ we can write:

$$\langle \lambda_j | M | \lambda_j \rangle = \langle 0 | 0_{\lambda_i} M \, 0_{\lambda_j}^\dagger | 0 \rangle \qquad \text{(IV. 11)}$$

The equation can be rewritten in terms of the double commutator defined above as:[13]

$$\langle \lambda_i | M | \lambda_j \rangle = \langle 0 [0_{\lambda_i}, M, 0_{\lambda_j}^\dagger] | 0 \rangle + (\tfrac{1}{2}) \langle 0 | [0_{\lambda_i}, 0_{\lambda_j}^\dagger] T | 0 \rangle$$

$$+ (\tfrac{1}{2}) \langle 0 | T [0_{\lambda_i}, 0_{\lambda_j}^\dagger] | 0 \rangle \qquad \text{(IV. 12)}$$

In the RPA approximation, the last two terms of (IV. 12) vanish because $[0_{\lambda_i}, 0_{\lambda_j}^\dagger] = \delta_{\lambda_i \lambda_j}$. Introducing $| HF \rangle = | 0 \rangle$ and evaluating the expectation value of the double commutator, we get:[13]

$$\langle \lambda_j | M | \lambda_j \rangle \approx \sum_{n\nu} \sum_{m\gamma} [Y_{n\nu}^*(\lambda_i) Y_{m\gamma}(\lambda_j) + Z_{n\nu}^*(\lambda_i) Z_{m\gamma}(\lambda_j)] \cdot$$

$$\cdot \, [T_{nm} \, \delta_{\nu\gamma} - T_{\gamma\nu} \, \delta_{nm}] \qquad \text{(IV. 13)}$$

which allows us to calculate excited state - excited state transition elements from the knowledge of the amplitudes Y and Z for excitations from the ground state.

Higher order approximations to the equations of motion have been proposed by McKoy et alt.,[12] and applied to the calculation of transition frequencies and oscillator strengths of several molecules.[14] Complete details of the derivations and results of the applications can be found in the cited literature.

References

1. D. J. Rowe, "Nuclear Collective Motion," Methuen and Co. Ltd., London, 1970, pag. 229.
2. See for instance, H. F. Schaefer III, "Electronic Structure of Atoms and Molecules, Addison-Wesley Publishing Co., 1972.
3. See for instance, J. N. Murrell and A. J. Harget, "Semi-empirical Self-Consistent-Field Molecular-Orbital Theory of Molecules," Wiley-Interscience, London, 1972.
4. See reference 1, pag. 245.
5. R. A. Harris, J. Chem. Phys., 50, 3947 (1969).
6. D. J. Thouless, Nucl. Phys., 22, 78 (1961).
7. R. D. Mattuck, "A Guide to Feynman Diagrams in the Many-Body Problem," McGraw Hill Book Co., New York, 1967, pag. 105.
8. L. D. Landau, E. M. Lifshitz, "Quantum Mechanics," Pergamon Press, London, 1958.
9. S. Raimes, "Many-Electron Theory," North-Holland Publishing Co., Amsterdam, 1972, pag. 21.
10. F. A. Berezin, "The Method of Second Quantization," Academic Press, New York, 1966.
11. T. Shibuya, J. Rose and V. McKoy, J. Chem. Phys., 58, 500 (1973).
12. T. Shibuya and V. McKoy, Phys. Rev. A, 2, 2208 (1970).
13. D. L. Yeagar, M. A. C. Nascimento and V. McKoy, accepted for publication, Phys. Rev. A.

14. J. Rose, T. Shibuya and V. McKoy, J. Chem. Phys., 58, 74 (1973); D. L. Yeagar and V. McKoy, ibid., 60, 2714 (1974); D. L. Yeagar, V. McKoy and G. A. Segal, ibid., 61, 755 (1974).

PROPOSITION I

An RPA calculation of nuclear shielding constants

Abstract

Since the expression for the nuclear shielding constant for diamagnetic molecules was developed by Ramsey, several attempts have been made to calculate this property for small systems. The main difficulty is the sum over all excited states and the continuum which is a characteristic of all properties derived by second-order perturbation theory. Several methods have been proposed in order to avoid the sum over states. Variational approaches have been proposed also. Besides that, a semi-empirical model has been proposed, where the nuclear shielding is calculated as a sum of various contributions. None of these methods is completely satisfactory although some calculations using one or other methods agree well with experiment.

We propose a solution where the sum over excited states plus integration over the continuum is replaced by an effective discrete summation over the states obtained by using the RPA (lower order EOM) method.

I. Introduction[1]

Suppose a nucleus is surrounded by electrons in a magnetic field of intensity $\vec{H}_{ext}$. If the nucleus has a magnetic moment $\vec{\mu}$, the energy of interaction between the system and the field due to this moment is:

$$\Delta E = -\vec{\mu}\,\vec{H}_{local} \qquad (1)$$

where

$$\vec{H}_{local} = \vec{H}_{ext}\,(1 - \sigma) \quad .$$

Equation (1) can be interpreted in the following way: since the nucleus is surrounded by electrons in motion, there will be besides the external field, $\vec{H}_{ext}$, another field $\vec{H}'$, proportional to $\vec{H}_{ext}$, due to this motion. If we write:

$$\vec{H}' = -\underset{\wedge}{\sigma}\,\vec{H}_{ext} \qquad (2)$$

the nucleus will experience a field,

$$\vec{H}_{local} = \vec{H}_{ext} + \vec{H}' = \vec{H}_{ext}\,(1 - \underset{\wedge}{\sigma}) \quad ,$$

and equation (1) is obtained, provided that $\vec{H}_{ext}$ is not too large.[2]

The quantity $\underset{\wedge}{\sigma}$ is called nuclear shielding or screening constant, but since $\vec{H}'$ does not have to be in the same direction of $\vec{H}_{ext}$, $\underset{\wedge}{\sigma}$ is generally a second-order tensor. For most applications the system is in rapid motion and the quantity actually measured is the average of $\underset{\wedge}{\sigma}$:

$$\sigma = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}) = \frac{1}{3} \mathrm{Tr}\, \underset{\sim}{\sigma} \quad ,$$

while the components can be measured in solids[3] and gases.[4]

The importance of calculating this quantity becomes obvious if we recall that it is this dependence on the local field in the electronic environment which makes NMR spectroscopy a powerful technique for structural analysis.

Suppose a nucleus, of spin quantum number 1/2 for simplicity, is in an external constant magnetic field, $\vec{H}_{ext}$. The interaction with the field will give rise to two different spin-states, of different energies, corresponding to the magnetic moments aligned parallel or antiparallel to the external field. In general, for a nucleus with spin quantum number I, there will be (2 I + 1) such states. Now, if another field, $\vec{H}_{osel}$, perpendicular to the original one is set oscillating at a frequency S, such that hS is equal to the energy spacing between the two levels, nuclei will absorb energy from $\vec{H}_{osel}$, and these transitions can be detected. This is the general basis of NMR spectroscopy.

In practice the resonance condition:

$$hS_N = g_N \beta_N \vec{H}_{ext} \tag{3}$$

can be achieved by varying the frequency of oscillation, S, or the external field, $\vec{H}_{ext}$. Technically it is easier to keep constant the frequency and vary the external field. The field variation is made by superimposing a very small secondary field to the primary strong external field, the secondary field providing a sweep of $\vec{H}_{ext}$.

The energy spacing depends on the value of $\vec{H}$ experienced by the nucleus, and hence nuclei with the same $\vec{\mu}$ can resonate at different frequencies since their electronic environment can be different causing different $\vec{H}_{local}$. In other words, the frequency of resonance (or the field of resonance) will be a function of the screening constant for the nucleus.

Practically in order to avoid the problem of always specifying both the magnetic field and frequency at which resonance occurs, it has become common to define a scale of "chemical shifts" for a nucleus relative to some standard compound containing the same nucleus. So, if $\vec{H}_{sample}$ is the value of the field, at a given frequency ν of $\vec{H}_{osl}$, for which a given nucleus resonates, and $\vec{H}_{ref}$ the resonance field for the same nucleus in a reference molecule, the "chemical shift", in parts per million, is defined by the relation:

$$\delta = \frac{\vec{H}_{ref} - \vec{H}_{sample}}{\vec{H}_{ref}} \times 10^{6} \qquad (4)$$

II. General theory of the nuclear shielding

Since the energy of interaction between the magnetic moment of the nucleus, $\vec{\mu}_N$, and the external magnetic field, $\vec{H}_{ext}$, is small, we can use second-order perturbation theory to derive an expression for $\hat{\sigma}$. The spin of the electrons can be neglected throughout the derivation because the magnetic shielding fields originated by them are much smaller than the contributions from orbital magnetic moment, as discussed by Van Vleck[5] and Wick.[6]

The quantum-mechanical equation for a particle of mass m and charge q in an external magnetic field, characterized by the vector potential $\vec{A}$, can be obtained from correspondence with classical mechanics if we remember that the momentum of the particle has to be replaced by[7]

$$\vec{p} = m\vec{v} - \left(\frac{q}{c}\right)\vec{A} \tag{5}$$

Using equation (5) the hamiltonian for a many-particle system in an external field will be:

$$\mathcal{H} = \sum_j \frac{1}{2m_j}\left\{\hat{p}_j - \frac{q_j}{c}A_j\right\}^2 + V \tag{6}$$

where V is the potential energy of the system.

The next steps involved in obtaining Schroedinger equation in a more conventional form are: (a) expansion of the square; (b) choice of a gauge for $\vec{A}$. Besides that, we will assume the Born-Oppenheimer approximation. With this last assumption, the masses and charges will be all equal in equation (6) ($m_j = m_{electron}$, $f_j = -e$) since the kinetic energy of the nuclei doesn't appear anymore.

Then expanding the square, taking the coulomb gauge, div $\vec{A} = 0$ (which is the more convenient for magnetostatic problems) and the Born-Oppenheimer approximation, we get:

$$\left\{ \sum_j \left[-\frac{\hbar^2}{2m}\nabla_j^2 + \frac{e\hbar}{imc}\vec{A}_j\cdot\vec{\nabla}_j + \frac{e^2}{2mc^2}\vec{A}_j^{\,2}\right] + V \right\}\Psi = E\Psi \qquad (7)$$

This is the time independent Schroedinger equation for a system of spinless particles in an external magnetic field described by $\vec{A}$, in the coulomb gauge and Born-Oppenheimer approximation.

To derive an expression for $\underset{\wedge}{\sigma}$ all we need to know is the contribution to the second order correction energy, due to the shielding. From equation (1) this contribution is:

$$\Delta E_S = \underset{\wedge}{\sigma}\,\mu\vec{H}$$

Then to obtain an expression for $\underset{\wedge}{\sigma}$ all we need is the part of the energy correction linear in $\mu\vec{H}$.

From equation (7) we can see that the perturbation can be written:

$$\mathcal{H}' = \frac{e}{mc}\sum_j \vec{A}_j\cdot\vec{p}_j + \frac{e^2}{2mc^2}\sum_j \vec{A}_j^{\,2} \qquad (8)$$

and from second-order perturbation theory we know that:

$$\Delta E^{(2)} = <0|\mathcal{H}'|0> + \sum_{n\neq 0} \frac{<0|\mathcal{H}'|n><n|\mathcal{H}'|0>}{E_0 - E_n} \qquad (9)$$

Now, for simplicity, we assume that the origin of the vector potential and the origin of the coordinates system coincide with the nucleus whose shielding is of interest. With these assumptions, the vector potential at electron j, $\vec{A}_j$, can be written:

$$\vec{A}_j = \tfrac{1}{2}(\vec{H}_{ext} \times \vec{r}_j) + \frac{\vec{\mu} \times \vec{r}_j}{r_j^3} \qquad (10)$$

where the first term is the vector potential at electron j distant $\vec{r}_j$ from the nucleus of interest, due to the external magnetic field, and the second term is the vector potential at the same electron due to the magnetic moment of the nucleus of interest.

Now let's make one further assumption that the field $\vec{H}_{ext}$ is along the Z axis. Taking into account all the above assumptions, substituting (9) in (10) and taking only terms linear in μ H, we get

$$\Delta E^{(2)}(\mu H) = \mu H\, \sigma_{zz} = \frac{e^2}{2mc^2}\, \mu H \sum_j <0|\frac{x_j^2 + y_j^2}{r_j^3}|0> -$$

$$\frac{e^2}{2mc^2}\, \mu H \left[\sum_{n\neq 0} \frac{1}{E_n - E_0} \left\{<0|\sum \hat{L}_{zj}|n>\right.\right.$$

$$<n|\sum_j \hat{L}_{zj}/r_j^3|0> + <0|\sum_j \hat{L}_{zj}/r_j^3|n>$$

$$\left.\left.<n|\sum_j \hat{L}_{zj}|0>\right\}\right] \qquad (11)$$

From (11) the σ_{zz} component can be calculated:

$$\sigma_{zz} = \frac{\Delta E^{(2)}(\mu H)}{\mu H} ,$$

with similar expressions for σ_{xx} and σ_{yy}. Taking the average over all orientations of the system, we get

$$\sigma_{av} = \frac{e^2}{3\,mc^2} \sum_j <0 \left| \frac{1}{r_j} \right| 0> - \frac{e^2}{3\,mc^2} \sum_{n\neq 0} \frac{1}{E_n - E_0} \left\{ <0 \left| \sum_j \hat{L}_j/r_j^3 \right| n><n \left| \hat{L}_j \right| 0> \right\} \tag{12}$$

This formula was first obtained by Ramsey.[8] The first term corresponds to the Lamb[9] expression for the diamagnetic shielding and the second is referred to as the high-frequency or paramagnetic contribution to the nuclear shielding.

We recall that Ramsey's formula is valid in the rather special case where the origin of the vector potential and the origin of the coordinate system coincide at the nucleus of interest. Chan and Das[10] developed a more general expression allowing for an arbitrary choice of the origin of the vector potential. The expression was further generalized by Raynes[11] for the case where the origin of coordinates, the gauge origin and the nucleus of interest are located at different points.

III. Calculation of the nuclear shielding constant

The calculation of the diamagnetic part of $\underset{\wedge}{\sigma}$ poses no problem and in fact it has been calculated for atoms since Lamb[9] developed the expression. For molecules it can also be calculated, the accuracy depending only on the quality of the ground-state wave function $|0>$. The great difficulty resides in the paramagnetic contribution which involves the knowledge of all excited states and the continuum.

The calculation of nuclear shielding has been the subject of several studies. We cite briefly some of the approaches. For a review of the theory and methods of calculation, the reader is referred to the papers by Lipscomb,[12] Musher,[13] O'Reilly,[14] Flygare[15] and Raynes.[11, 16]

Methods involving gauge transformation have been explored by Kern and Lipscomb,[17] Sadley,[18] Kurita and Ito,[19] Chan and Das,[10] and Hameka,[20] in an attempt to cancel or minimize the paramagnetic term. In general the results are good only for protons in diatomic and triatomic molecules.

A variational method was introduced by Tillieu and Guy[21] where the trial wave function has an explicit dependence on $\vec{H}_0$. The same form of function was used by Das and Bershon[22] to the calculation of $\underset{\wedge}{\sigma}\, H_2$. While the method seems to give reasonable results for diatomic molecules, it fails when the wave function has nodes. Another type of trial wave function was introduced by Ishiguro and Koide[23] to calculate magnetic properties of H_2, with reasonable results. Karplus and Kolker[24] developed a variation-perturbation method and used it to calculate magnetic susceptibilities and shielding constants for diatomic molecules. The method is good for H, F and Li nuclei but fails for other nuclei. Again care is required if the wave function has nodes.

Perturbed Hartree-Fock theories have been developed by Lipscomb et al.[25] and applied to $^1\Sigma$ diatomic molecules, and by Pople et al.[26] for diatomic and small polyatomic molecules. Some of the results are in agreement with experimental data.

From all the methods proposed the best results are obtained by perturbed Hartree-Fock theory, which means a lot of computational effort and, at least for the moment, impossibility of studying larger systems.

Proposition

We propose a different approach where, starting from Ramsey's expression, the summation over excited states and integration over the continuum is to be replaced by an "effective" summation over a discrete spectrum obtained with a RPA (lower EOM)[27] calculation.

The spectrum generated by a RPA calculation has some features that encourage us to use it in the study of second-order magnetic properties, like nuclear shielding constants. It was shown a long time ago by Dalgarno and Lynn[28] that if a given set of oscillator strengths for a given system satisfies the oscillator strengths sum rules, this set can be used to obtain accurate values of these properties which can be written as sums of oscillator strengths. More recently Harris[29] has shown that the RPA method satisfies the oscillator strengths as well as rotational strengths sum rules. Recently, a good test to the validity of these arguments and applicability of the RPA approximation to the calculation of these properties has been provided by Martin et al.[30] These authors used the RPA approximation and a direct sum over states to calculate second-order dipole properties and van der Waals coefficients, using a basis set expansion and no continuum like wave functions. Results reported for H_2 and He are in excellent agreement with experimental results and other extensive calculations.

The ability of the RPA approximation to reproduce those second-order properties using a discrete basis set encourages us to investigate its applicability to second-order magnetic properties. Although there is no sum-rule equivalent for the nuclear shielding and other second-order magnetic properties, we believe that the RPA method provides us with a good set of matrix elements and excitation energies, such that the complete sum over states and integration over the continuum can be "effectively" replaced by a discrete summation. This is basically the philosophy of the EOM method, namely, to get good matrix elements without trying to construct elaborate wave functions.

Initially we would perform calculations on small diatomic molecules for which good experimental results are known, and then depending on the success of the method the calculations would be extended to other small molecules. An interesting application should be BH ($^1\Sigma$) surprisingly found by Lipscomb[31] to be paramagnetic, although no experiments are yet available for comparison. But we have to consider that the result by Lipscomb may be due to a bad description of BH molecule in the Hartree-Fock treatment.[33]

Since we use as zero-order a RH wave function, the method as it stands now would not be applicable to large molecules, but a success of the method for small molecules would encourage us to semi-empiricize the method such that it could accept, for instance, CNDO/2 wave functions. That would be another good test for the RPA method, since it is known that the EOM matrix-elements are particularly insensitive to the approximate ground state used to set up them.[32]

Finally we want to comment that magnetic susceptibilities can be calculated simultaneously since all the matrix elements necessary to its calculation are used to calculate the nuclear shielding constant.

References

1. J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw Hill Book Co., Inc., New York, 1959; D. W. Davies, "The Theory of the Electric and Magnetic Properties of Molecules", John Wiley & Sons, London, 1967.
2. N. E. Ramsey, Phys. Rev. (A), **1**, 1320 (1970).
3. R. W. Vaughan, in "Annual Reviews in Materials Science", Vol. 4, Edited by R. A. Huggins, R. H. Bube and R. W. Roberts, 1974, and references therein; L. B. Schreiber and R. W. Vaughan, Chem. Phys. Letters, **28**, 586 (1974).
4. G. Graff, Z. Physik., **155**, 433 (1959).
5. J. H. Van Vleck, "Electric and Magnetic Susceptibilities", Oxford University Press, London, 1932.
6. G. C. Wick, Phys. Rev., **73**, 51 (1948).
7. J. C. Slater, "Quantum Theory of Atomic Structure", Vol. I, p. 418, McGraw Hill Book Co., Inc., New York, 1960.
8. N. F. Ramsey, Phys. Rev., **78**, 699 (1950.
9. W. Lamb, Phys. Rev., **60**, 817 (1941).
10. S. I. Chan and T. P. Das, J. Chem. Phys., **37**, 1527 (1962).
11. W. T. Raynes, in "Nuclear Magnetic Resonance", ed. R. K. Harris, **3**, 1 (1974).
12. W. N. Lipscomb, in "Advances in Magnetic Resonance", **2**, 137 (1966), ed. J. S. Waugh, Academic Press, New York.
13. J. I. Musher, ibid., **2**, 177 (1966)

14. D. E. O'Reilly, in "Progress in Magnetic Resonance Spectroscopy", 2, 1 (1967), eds. J. W. Emsley, J. Freeney and L. H. Sutcliffe, Pergamon Press, London.

15. W. H. Flygare, Chem. Rev., 74, 653 (1974).

16. W. T. Raynes, in "Nuclear Magnetic Resonance", 1, 1 (1972), ed. R. K. Harris, The Chemical Society, London; ibid., 2, 1 (1973).

17. C. W. Kern and W. N. Lipscomb, J. Chem. Phys., 37, 260 (1962).

18. A. J. Sadlej, Mol. Phys., 19, 749 (1970).

19. Y. Kurita and K. Ito, J. Am. Chem. Soc., 82, 296 (1960).

20. H. G. Hameka, "Advanced Quantum Theory", p. 157, Addison-Wesley, Reading, Mass., 1965.

21. J. Tillieu and G. Guy, J. Chem. Phys., 24, 1117 (1956); Compt. Rend., 239, 1203 and 1238 (1954); ibid., 240, 1402 (1955); ibid, 241, 382 (1956); ibid., 242, 1279 (1956); ibid., 246, 574 (1958).

22. T. P. Das and R. Bershon, Phys. Rev., 104, 849 (1956).

23. E. Ishiguro and S. Koide, Phys. Rev., 94, 350 (1954).

24. M. Karplus and H. J. Kolker, J. Chem. Phys., 38, 1263 (1963); H. J. Kolker and M. Karplus, ibid., 41, 1259 (1964).

25. R. M. Stevens, R. M. Pitzer and W. N. Lipscomb, J. Chem. Phys., 38, 550 (1963).

26. J. A. Pople, J. W. McIver and N. S. Ostlund, J. Chem. Phys., 49, 2960 (1968); R. Ditchfield, D. P. Miller and J. A. Pople,

ibid., 53, 613 (1970).

27. T. I. Shibuya and V. McKoy, Phys. Rev. A, 2, 2208 (1970); T. I. Shibuya, J. B. Rose and V. McKoy, J. Chem. Phys., 58, 74 (1973); ibid., 58, 500 (1973).
28. A. Dalgarno and N. Lynn, Proc. Phys. Soc., 70, 802 (1957).
29. R. A. Harris, J. Chem. Phys., 50, 3947 (1969).
30. P. H. S. Martin, W. H. Henneker and V. McKoy, J. Chem. Phys., 62, 69 (1975).
31. R. Hegstrom, R. M. Stevens and W. N. Lipscomb, J. Chem. Phys., 45, 2378 (1966).
32. D. J. Rowe, 'Nuclear Collective Motion", Methuen and Co. Ltd., London, 1970, p. 247.
33. R. J. Blint and W. A. Goddard III, Chem. Phys., 3, 297 (1974).

PROPOSITION II

An investigation of the effect of σ correlation in the ordering of excited singlet states of polyenes

Abstract

Until recently the ordering of the excited singlet states of polyenes seemed to be well established. Recent experiments as well as theoretical calculations seem to indicate the existence of a low-lying ${}^1A_g$ state (trans-polyenes) other than the well established ${}^1B_u$ state. On the other hand, another set of experiments and calculations seem to support the original ordering.

Experiments are in progress in an attempt to clarify the situation. A more complete theoretical treatment is necessary in order to understand the origin of the theoretical controversy as well as to understand which factors are important to consider, if we want a good theoretical model to describe the spectra of these molecules.

We propose to investigate the importance of σ correlation energy in determining the ordering of the excited states of these compounds.

I. Introduction

Polyenes have been the subject of intensive studies since Hausser and coworkers first performed a detailed spectroscopic study of these compounds.[1] His work has been reviewed by Mulliken,[2] Maccoll,[3] Bayliss[4] and Plat.[5] Most of the earlier theoretical and experimental work was done in the period between 1930-1950. The interest in the subject was reactivated in the 1960's from a desire to understand the spectral and photochemical properties of the visual pigments, where polyene chains play an important role as chromophores.[6]

The main conclusions that came out from Hausser's work are: (a) the linear polyenes all have a strong transition in the near ultraviolet or visible with an oscillator strength varying between 1 or 2, and increasing in magnitude with chain length; (b) the excitation energy varies with increasing chain length converging to an asymptotic value of about 18,000 cm^{-1}; (c) the fluorescence spectra of some of the compounds showed approximately the same vibrational structure and intensity pattern as the absorption spectra, while for others there is a separation between the first peaks in absorption and emission, with this spacing tending to increase with the number of double bonds; (d) fluorescence and absorption spectra display different spectral shifts when the polyene is transferred from one solvent to another. While fluorescence is practically unaffected, the absorption, for instance for diphenyl polyenes, occurs at lower energies as the solvent polarizability increases.

Early theoretical descriptions[7] using either FEMO[8] or LCAO-MO[2] yield qualitatively correct results. In the free-electron molecular model the resulting orbitals alternate symmetry (A_g, B_u, A_g...) as energy increases. LCAO-MO results predict a ground-state of A_g symmetry followed by a B_u and two other A_g states. Then both models explain the strong allowed transition (${}^1A_g \rightarrow {}^1B_u$) and the lower intensity of the next higher singlet transition (${}^1A_g \rightarrow {}^1A_g$), although they differ in the ordering of the third and higher excited states. In their simplest form both FEMO and LCAO-MO fail to account for the energy gap for the first transition as the chain length increases. Both models predict a zero gap, although in the FEMO model the inclusion of a sine wave to the potential well gives a constant energy gap but still in poor agreement with experimental results. Valence bond calculations have been performed also.[9] These calculations predict a low-lying excited state of A_g symmetry in conflict with FEMO and LCAO calculations. But these VB calculations are inexpressive since both ground and first excited states have been represented by covalent structures, while the singlet excited state is almost certainly expected to be dominated by ionic structures.

Then, until recently, the ordering of the singlet excited states seemed to be well established and understood even by using very simple theories.

Recent experiments suggested the existence of a low-lying excited state of ${}^1A_g$ symmetry. Some theoretical results tend to support its existence while some other calculations, as well as experimental results, tend to contradict it.. We proceed with a brief account of these results. For a recent review the reader is referred to the paper by Hudson and Kohler,[10] although these authors, being advocates of the existence of this new state, tend to emphasize the experimental evidences which suggest its existence.

II. Recent Experiments and Theoretical Results

It seems that the whole story began with Hudson and Kohler's experiment in the α, ω diphenyloctatotraene (DPO).[10] Their high resolution optical absorption and emission spectra in crystal matrices at the liquid helium temperature indicate a transition to a singlet state-excited state at lower energy than the strong ${}^1A_g \rightarrow {}^1B_u$ transition. The transition to the "discovered" state is only weakly allowed (f = 0. 06 relative to f = 1. 5 for the ${}^1A_g \rightarrow {}^1B_u$ π-π^* transition). In an accompanying paper, Shulten and Karplus[11] presented PPP-CI calculations on the all trans butadiene, hexatriene and octatetraene. These authors showed that if in addition to single excitations, double excitations are included in the CI, there is a reordering of the states, the lowest-lying singlet being now of A_g symmetry. With this reordering the weak transition in DPO could be understood on a basis of a forbidden transition ${}^1A_g \rightarrow {}^1A_g$. They concluded that this transition should be a characteristic of all polyenes and related compounds.

That reordering has been noted some time ago by Koutecký[12] in going from a single to a full PPP-CI calculation on the same compounds. Thus the real contribution from Schulten and Karplus was to show that the ordering of states obtained with a full PPP-CI is the same as the one obtained with a S + D CI (single + double excitations). The relative energies cannot be compared because of the difference in parametrization.

In another experiment Moore and Song[13] measured the DPO excitation and fluorescence spectra and their polarization, at 77°K. They observed a weak low-lying transition which they interpreted as resulting from dimeric stacking of the DPO molecules. They report that many polyenes form aggregates at concentrations as low as 10^{-6} M, and that these aggregates are responsible for the weak transition observed. If their interpretation is correct that could be the cause for the weak transition observed by Hudson and Kohler, since the DPO concentration used was high enough to allow for the formation of these aggregates.

More recently, two photon absorption studies of DPO have been performed.[14] The preliminary results seem to indicate the existence of a state ^1A_g below the allowed ^1B_u. Again the concentration of DPO was high enough to allow formation of aggregates, but besides that, the authors themselves seem to agree that the results must be examined more carefully.[15]

Even considering that the weak transition in DPO is due to a forbidden transition $^1A_g \rightarrow {}^1A_g$, this by no means implies that a similar transition should be observed in all polyenes, mainly those without bulky substituents like phenyl groups.

In fact, 1, 3 butadiene has been studied experimentally by several authors and no evidence of a low-lying ^1A_g state has been found, while the existence of one such state slightly above the ^1B_u has been observed (see Table II).

Electron impact spectra of 1, 3 butadiene[16] and 1, 3, 5 hexatriane[17] have been reported recently. No transition $^1A_g \rightarrow {^1A_g}$ was observed below the $^1A_g \rightarrow {^1B_u}$ for butadiene.

More recently, Gavin and Rice[18] presented data from vacuum-ultraviolet spectra of cw and trans 1, 3, 5 hexatriane. They did not observe any low-lying band that could be attributed to a symmetry forbidden $^1A_g \rightarrow {^1A_g}$ transition. They carried out an analysis of the spectrum, determining positions, intensities and widths for the absorption bands of both isomers. Besides that, they performed a PPP-CI calculation using different parametrizations, and with single and single + double excitations. The reordering of states with the S + D excitations was again observed, but a much better agreement between experiment and calculation was obtained with a single excitation calculation. The authors reported that further work on octatetraene was in progress, and we have been informed that again no band for the new state was observed.[19]

At this point it seems that ab-initio calculations of these molecules are more than justified, and in fact some calculations for butadiene have been reported, but not for any higher member of the series.

Buenker and Whitten[20] performed ab-initio calculations for butadiene using a minimum basis set (fixed-group lobe GTO), including single excitations, S + D, and full CI treatment. When S + D excitations were included they noted the reordering of states similar to the one predicted by PPP-CI treatments, the main feature being the appearance of a low-lying ^1A_g state before the ^1B_u. However, in all CI's the transition energies are in complete disagreement with experiments.

Shih et al.[21] improved the basis set used by Buenker and Whitten by decomposing some of the fixed groups and adding diffuse $3p\pi$ functions at each carbon atom. These authors noted that when some σ core relaxation is allowed, a full π-CI gives a low-lying ^1B_u state followed by a ^1A_g state, but with transition energies still high by ~0.5 eV.

More recently Hosteny et al.[22] performed an extensive CI calculation for butadiene, which can be characterized as a full π-CI with a frozen SCF σ core. While some triplet states are in good agreement with experiment, the singlets show again the reverse order, and the transition energies not in agreement with experiments.

III. Discussion and Proposition

The use of approximate schemes like the PPP method and others has achieved a high degree of popularity because of its simplicity and the possibility of its application to the calculation of large systems.[23] However the results have to be examined carefully. In the specific case which we are dealing with now, the various PPP calculations used different parameters. For instance, Schulten and

Karplus[11] used a linear approximation for the resonance integrals[24] and the Ohno[25] formula for the electron repulsion integrals, and the program parameters were obtained by fitting single excitation results to the spectral data. Gavin and Rice[18] used the same approximation for the resonance integrals but the Mataga-Nishimoto[26] formula for the electron repulsion integrals. The parameters were scaled to reproduce excitations for benzene, hexatriene and octatetraene. Koutecký[12] studied in detail how the ordering of states is affected by a choice of the approximate formula for the electron-repulsion integrals. Of course, the energy of the states in a simple PPP calculation is a function of all parameters, but the reordering due to the CI is mainly dependent on the choice of the electron-repulsion integral approximation, which determines the correlation energy. These integrals can be written as a function of the internuclear distance

$$\gamma_{ij} = \gamma(R_{ij}) \tag{1}$$

He concluded that for a given molecule, correlation effects will be more pronounced if the function (1) is a more steeply decreasing function of the interatomic distance. According to this conclusion large correlation effects are expected in the Mataga approximation than in the original PPP. Still larger correlation effects will be obtained if the integrals were calculated theoretically using Slater orbitals. The calculations by Koutecký showed a general tendency for a low-lying g state to be shifted to lower energies, to a greater extent, upon extension of the CI, than the lowest u state. This result suggests that it is possible to find a set of realistic parameters such that, even with a full CI, the g state will not be shifted below enough to be the first singlet excited state. In fact that has been recently shown for butadiene, by Shinoda et al.[27] These authors used a resonance integral approximation proportional to the overlap integral and a Mataga-Nishimoto like-approximation for the repulsion integrals. The parameters were adjusted to fit transitions in benzene. Three different CI's were performed and in all cases, including the ones with S + D excitations, the ${}^1B_u$ state was found below the $2\,{}^1A_g$, and in one of the treatments including S + D excitations, the transition energies for these two states are in good agreement with experiments.

It is clear from the exposed above that approximate π electron theories, as they stand now, cannot give an answer to this problem. It is unfortunate that simple theories which can be applied to the calculation of large systems, present such ambiguities. Recently, Freed[28] decided to attack the problem of putting purely semi-empirical theories in a more theoretical basis, trying to define a true effective Hamiltonian and true parameters. There are many questions to be answered yet, but the approach is very interesting and promising.

Now let us turn our attention to the few ab-initio calculations performed up to now. Before that, one word about the quality that can be expected from these calculations. First of all, the choice of a good basis set is of fundamental importance. Secondly, the CI procedure has to be built in such a way that, within the limitations of time, money, etc., it includes the main correlation features necessary to describe a given state.

The basis set used by Buenker and Whitten[20] is much too contracted, restricting its ability to describe different states with different characteristics. Besides that, the CI treatment only correlated the four π orbitals and the highest σ occupied orbital. Following the authors, the idea of including single $\sigma \rightarrow \pi^*$ besides $\pi \rightarrow \pi^*$ excitations was suggested by the small energy difference between that orbital and the occupied π orbitals. No diffuse functions were included in the basis set and that was pointed out by other authors[21] as one of the main reasons for the failure of the calculations, but we want to comment on this later.

Shih et al.[21] decomposed the original basis set of Buenker and Whitten in different ways, obtaining much more flexible basis sets. For the calculation of $\pi \rightarrow \pi^*$ excited states $3p\pi$ diffuse functions were added to each carbon atom. A full CI treatment was undertaken where only the π MO's were allowed variable occupation. The results of these calculations still showed the $2\,^1A_g$ state appearing below the ^1B_u. The best results were obtained using a full π-CI (PCMO), where the excited orbitals used in the CI expansion are the ones obtained by the SCF treatment of the parent configuration. With that procedure the $1\,^1B_u$ state appeared below the $2\,^1A_g$ state, but both transition energies are still high by ~ 0.5 eV. The most important fact to be noted is that the energy of $2\,^1A_g$ state did not change at all with the CI (PCMO) while the $1\,^1B_u$ state was lowered by 0.3 eV. Since this procedure allows some σ core relaxation, that suggests its importance in the description of the ^1B_u state. One interesting question which emerges from these results is how much of the improvement obtained was due to a better basis set and to the σ core relaxation. Based only on these results all we can say is that both effects are equally important.

Now let us see what happens if we try to improve even more the basis set without taking care of σ correlation. The answer for that can be found in the most recent calculation of butadiene, by Dunning et al.[22] These authors used a double-g contracted GTO's basis set plus two diffuse $2p\pi$ functions on each carbon atom. A full π-CI with frozen SCF σ core was carried out. The results for the two low-lying singlets of B_u symmetry are higher by 1 eV and the $2\,^1A_g$ appears ~ 0.3 eV below the $1\,^1B_u$ state. The results of some of these calculations are presented in Table II.

It seems evident by now that no reliable calculation for the singlet states of butadiene has ever been done, since an important factor, namely σ correlation, has been practically neglected. The importance of σ correlation for the description of singlet B_u states can be seen also from a VB point of view. First we should expect a good similarity, between V and T states of butadiene and ethylene. Now, while in the MO-CI picture the V and T states of ethylene are isoconfigurational singlet and triplet arising from $\Sigma_{core}\,\pi_u\pi_g^*$, the V state is purely ionic $(1/\sqrt{2})\,[\Delta_{a\bar{a}} - \Delta_{b\bar{b}}]$ and the T state is purely covalent $(1/\sqrt{2})\,[\Delta_{a\bar{b}} - \Delta_{b\bar{a}}]$ in the VB method. Therefore it is to be expected that the effect of the readjustment of the σ electrons in the V state is much larger than in T and N states. A recent VB calculation of butadiene by Campion and Karplus[29] shows that only ionic structures contribute for states of B_u symmetry.

Before putting the proposition in a final defined form, we want to comment on the use of diffuse functions to describe these ^1B_u states. Since most of the SCF calculations use of Roothaan approximation to the Hartree-Fock model, the use of extended basis sets of AO's, shall in principle give better results. Of course the infinite expansion would be equivalent to the Hartree-Fock equations. But since this is unpractical we hope to find a finite optimized basis which gives us a Hartree-Fock or near Hartree-Fock results, and then include correlation effects. Then double-δ and extended basis sets are necessary for a good description of the molecular systems, since minimal basis sets give, in general, a poor description even of the ground state.

The use of diffuse functions has been shown to be important in the description of the V state of ethylene.[30, 31] Now, since butadiene can be viewed as formed by two ethylene units, we should expect the V state of this compound (as well as for higher polyenes) to be similar in character. There is no question about the importance of these diffuse functions. But one thing we would like to know is how diffused they really need to be in order to give a good description of these states. This is an important point because the use of these diffuse functions, while giving better results, gave rise to a question about the character of these states.

In some of these calculations for the ethylene molecule where diffuse pπ functions have been used,[30-32] the resultant V state is very diffuse (Rydberg-like) while the T state is always valence-like. Other calculations which do not use standard CI techniques predict both states being valence-like.[33-35] Table I shows some of the calculations with their principal characteristics and results. The experimental results seem to confirm the valence character of the V state.[36] Let us see if it is possible to understand why some of the CI calculations generate a Rydberg-like V state. At least for two of such calculations, where a full π-CI with σ-core relaxation has been done,[30,31] the lack of a good treatment of σ correlation energy, could be responsible for such diffuseness. But in the calculation by Bender et al.,[32] all the S + D excitations, including those from the three highest occupied σ orbitals, were considered and they still got a diffuse V state. While the inclusion of σ correlation reduced the second-moment of the π_g^* orbital ($\langle \alpha^2 \rangle$) from 49.1 to 35.4 bohr^2, it is improbable that the inclusion of higher excitations would contract this orbital to such an extent as to give a valence character to the state. So, it seems that this diffuse character is being forced by the use of such high diffuse pπ functions.

Now a short comment on two of the calculations in Table I which used diffuse functions and predicted a valence character to the V state. First, in the work by Ryan and Whitten[33] the diffuse functions added are not so diffuse as in the calculations by Bender et al. Besides that, the particular process of getting the σ^* orbitals to be used in the CI expansion makes impossible a direct comparison between this calculation and the one by Bender et al., in respect to the balance of σ correlation versus use of diffuse functions. But the importance of mixed $(\sigma \rightarrow \sigma^*)$ $(\pi \rightarrow \pi^*)$ excitations was so evident in the work by Ryan and Whitten that it led Mulliken[37] to use it as an argument about the possibility of the V state being, in reality, a mixed $V\sigma$ $V\pi$ state. The failure of the calculation by Dunning et al.[22] on butadiene gives some support to this argument. About the calculations of Rose et al.,[35] again since, at least for the moment, there is no established correspondence between the RPA, HRPA and standard CI techniques, nothing can be learned from those calculations about the balance of σ correlation versus diffuse functions in CI calculations.

Then, the proposition consists of a careful study of σ correlation and the use of diffuse functions in the description of the V state of ethylene and butadiene, using standard CI techniques. For ethylene we are more concerned about the diffuse character of this state predicted by CI calculations, while in butadiene besides the diffuse character, the reverse order of the singlet states has to be clarified. Another interesting point to be checked is how effective a tight d function compared with diffuse $p\pi$ function, would be in providing a good basis to describe the correlation effects. What we can learn from these studies will be important to understand the properties of higher polyenes.

Table I. Some calculations of the V and T states of ethylene

Type of calculation	Basis Set[a]	Exponent of diffuse functions for V state	N-V transition energy (eV)[b]	N-T transition energy (eV)[b]	Second moment for V state (bohr^2)	Ref.
Complete π-CI with σ core relaxation	[4s 3p/2s] + diffuse 2pπ GTO's	$g_1 = 0.0365$, $g_2 = 0.0116$, $g_3 = 0.0037$	8.28	4.22	41.4570	30
Partial π-CI with σ core relaxation	[5s 3p/1s] which includes s and p diffuse function GLO's	$g_d = 0.02$	8.32	4.25	-	31
Partial ($\pi + \sigma$) CI. Multiconfigurational calculation using iterative natural orbital procedure	[4s 2p/2s] + diffuse 2p function GTO's	$g_1 = 0.0250$ $g_2 = 0.0077$	-	-	35.4	32
Partial ($\pi + \sigma$) CI	Fixed groups of GLO's + p and d functions	$g_{p\pi} = 0.06$, $g_{d_{xz}} = 0.2$, 0.6 $g_{d_{yz}} = 0.2$	8.02	4.98	8.2873	33
Partial ($\pi + \sigma$) CI	Minimum basis set of STO's + 2 diffuse 3pπ	$g_1 = 1.1$ $g_2 = 0.55$	8.0	3.9	~7.5	38
RPA	[4s 2p/2s] + 2pπ diffuse GTO's	$g_1 = 0.0365$, $g_2 = 0.0116$, $g_3 = 0.0037$	7.46	-	7.47[c]	34
HRPA	same as above	same as above	7.9	4.1	9.0	35

Table I (continued)

[a] For the case of GTO's the contractions referred to the gaussian sets of Huzinaga.

[b] Experimental transition energies: (N → V) = 7.6 eV, (N → T) = 4.6 eV (vertical transition energies).

[c] From a natural orbital analysis.

Table II. Results of ab-initio calculations of some transition energies for trans 1,3 butadiene (in eV)

State	Theoretical Results				Experimental Results			
	Buenker + Whitten[a]	Shih et al.[b]	Hosteny et al.[c]	Campion + Karplus[d]	Optical	Trapped Electron[e]	Ion Impact[f]	Electron Impact[g]
$1\,^3B_u$	4.35	3.24	3.45	-	3.22[h]	3.3	3.2	3.22 ± 0.04
$1\,^3A_g$	6.22	4.95	5.04	-	-	-	4.9	4.91 ± 0.03
$1\,^1B_u$	10.34	6.60	7.05	9.68	5.92[i]	~6	6.1	5.92 ± 0.02
$2\,^1A_g$	7.71	6.67	6.67	4.71	6.25[j]	-	-	-
$2\,^1B_u$	-	7.98	8.06	-	7.27[i]	7.2	7.3	7.09 ± 0.02
$2\,^3B_u$	9.23	7.55	7.14	-	-	-	-	-

[a] Ref. 20.

[b] Ref. 21.

[c] Ref. 22.

[d] Ref. 29.

[e] H. H. Brongersma, J. A. van der Hart and L. J. Oosterhoff, in "Fast Reactions and Primary Processes in Chemical Kinetics", ed. S. Cleasson, Interscience, New York, 1967, p. 211.

[f] J. H. Moore Jr., J. Phys. Chem., 76, 113 (1972).

Table II (continued)

[g] Ref. 16.

[h] D. F. Evans, J. Chem. Soc. (London) 1735 (1960).

[i] L. C. Jones Jr. and L. W. Taylor, Anal. Chem. 27, 228 (1955).

[j] W. C. Price and A. D. Walsh, Proc. Roy. Soc. London, 174, 220 (1940).

References

1. K. W. Hausser, K. Kuhn, A. Smakula, M. Hoffer and K. H. Kreuchen, Z. Physik. Chem., B29, 363, 371, 378, 384, 391 417 (1935).
2. R. S. Mulliken, J. Chem. Phys., 7, 364 (1939).
3. A. Maccoll, Quart. Rev., 1, 16 (1974).
4. N. S. Bayliss, Quart. Rev., 6, 319 (1952).
5. J. R. Platt, in "Radiation Biology", Vol. 3., ed. Daniel Davy, Hartford, 1956.
6. B. Honig and T. Ebrey, Ann. Rev. Biophys. Bioeng., 3, 151 (1974).
7. See for instance, J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules", Chapman and Hall, London, 1963; H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules", Academic Press, New York, 1967; L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, 1966.
8. N. S. Bayliss, J. Chem. Phys., 16, 287 (1948); H. Kuhn, ibid., 16, 840 (1948); H. Kuhn, ibid., 17, 1198 (1949); H. Kuhn, Helv. Chim. Acta, 31, 1441 (1948); F. Bar, W. Huber, G. Handschig, H. Martin and H. Kohn, J. Chem. Phys., 32, 470 (1960).
9. A. L. Sklar, J. Chem. Phys., 5, 669 (1937).
10. B. S. Hudson and B. E. Kohler, Chem. Phys. Lett., 14, 299 (1972).

11. K. Schulten and M. Karplus, Chem. Phys. Lett., 14, 305 (1972).
12. J. Koutecký, J. Chem. Phys., 47, 1501 (1967).
13. T. A. Moore and P. S. Song, Chem. Phys. Lett., 19, 128 (1973); T. A. Moore and P. S. Song, Nature NB, 243, 30 (1973).
14. R. L. Swofford and W. M. McClain, J. Chem. Phys., 59, 5740 (1973).
15. W. A. Goddard III, personal communication.
16. O. A. Mosher, W. M. Flicker and A. Kuppermann, J. Chem. Phys., 59, 6502 (1973).
17. E. W. F. Knoop and L. J. Oosterhoff, Chem. Phys. Lett., 22, 247 (1973).
18. R. M. Gavin and S. A. Rice, J. Chem. Phys., 60, 3231 (1974).
19. W. A. Goddard III, personal communication.
20. R. J. Buenker and J. L. Whitten, J. Chem. Phys., 49, 5381 (1968).
21. S. Shih, R. J. Buenker and S. D. Peyerimhoff, Chem. Phys. Lett., 16, 244 (1972).
22. T. H. Dunning Jr., R. P. Hosteny and I. Shavitt, J. Amer. Chem. Soc., 95, 5067 (1973).
23. See, for instance, J. N. Murrell and A. J. Harget, "Semi-empirical Self-consistent-field Molecular-orbital Theory of Molecules", Interscience, London, 1972.
24. B. Ross and P. C. Skancka, Acta Chem. Scand., 21, 233 (1967).
25. K. Ohno, Theoret. Chim. Acta, 2, 219 (1964).
26. N. Mataga and K. Nishimoto, Z. Physik. Chem. (Frankfurt),

13, 140 (1957).

27. H. Schinoda, H. Tatematsu, T. Miyazaki, Bull. Chem. Soc. Jap., 46, 2950 (1973).

28. K. F. Freed, J. Chem. Phys., 60, 1765 (1974); S. Iwata and K. F. Freed, 61, 1500 (1964).

29. W. J. Campion and M. Karplus, Molec. Phys., 25, 921 (1973).

30. T. H. Dunning Jr., W. J. Hunt and W. A. Goddard III, Chem. Phys. Lett., 4, 147 (1969).

31. R. J. Buenker, S. D. Peyerimhoff and W. E. Kammer, J. Chem. Phys., 55, 814 (1971).

32. C. F. Bender, T. H. Dunning Jr., H. F. Schaefer III, W. A. Goddard III and W. J. Hunt, Chem. Phys. Lett., 15, 171 (1972).

33. J. A. Ryan and J. L. Whitten, Chem. Phys. Lett., 15, 119 (1972).

34. T. H. Dunning Jr., Ph.D. dissertation, California Institute of Technology, 1970.

35. J. Rose, T. Shibuya and V. McKoy, J. Chem. Phys., 58, 74 (1973).

36. P. G. Wilkinson, Can. J. Phys., 34, 643 (1956); E. Miron B. Raz and J. Jortner, Chem. Phys. Lett., 6, 563 (1970).

37. R. S. Mulliken, Chem. Phys. Lett., 25, 305 (1974).

38. K. Tanaka, Inter. J. Quantum Chem., 6, 1087 (1972).

Proposition III

Abstract

β-Diketones are well known to exist in a keto-enol tautomerism. In these compounds the enol form is stabilized by a strong hydrogen bond. The nature of this hydrogen bond has been the subject of extensive studies, and some models have been proposed to account for its properties.

We propose to study these compounds using high-resolution solid state PMR. We believe that the results obtained by this technique could bring some new evidences for the understanding of the nature of the hydrogen bond.

β-Diketones are well known to exist in a keto-enol tautomeric equilibrium:

The existence of both forms can be clearly demonstrated by PMR where two distinct pmr signals are observed.[1,2] In some cases (for instance, $X=Y=CH_3$ and $R=CN, NO_2, SCN$) the total enolization has been observed by the absence of signal for the CHR group.[3] The intramolecular nature of the hydrogen bond in (E) form can be proved by studies of the H-bridged chemical shift dependence on solvent and in solvent concentration. It has been shown that, provided the solvent is not too basic, the chemical shift of that proton is independent of concentration and solvent system.[2] The formation of the hydrogen bond can also be characterized by infra-red spectroscopy where a broad band is observed in the region of -CH stretching.

The nature of the intramolecular hydrogen bond in the enol tautomer has received considerable attention. One of its interesting aspects is related to the chemical shift of the proton participating in the hydrogen bond. In acetylacetone (2,4-pentanedione) the chemical shift for this proton occurs at $\sim$15.4 ppm relative to TMS (tetramethylsilane) and depending on the substituents, it can be shifted even more to down field. For instance, in case X=Y=ϕ and R=H, the chemical shift is ~17 ppm. This means that these protons are very disshielded. In some cases these chemical shifts show a temperature dependence which suggests that more than one state with different chemical shifts for the bridged hydrogen exist in equilibrium.

One of the most important questions to be answered is whether the hydrogen bond in the enol tautomer is best described as a vinyl alcohol group hydrogen-bonded to a carbonyl oxygen or whether the potential function for the proton motion is a double minimum.

Many authors[2,4-6] have tried to explain this large downfield chemical shift, assuming that the bridged proton moves in a double minimum potential, and due to the possibility of tunnelling the chemical shift would be formed by two different contributions:

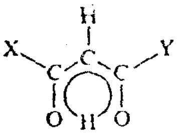
$$\delta_H = P_1 \delta_1 + P_2 \delta_2$$

where P_1 and δ_1 are the chemical shift and probability of the proton being in the first potential well and P_2 and δ_2 for the second potential well.

Acetylacetone has been theoretically studied by several authors[7-9] and the existence of a double minimum seems to be confirmed. But, for instance, if we take X=Y=CF_3, the potential does not show a double minimum.[8] For this case the chemical shift is ~13 ppm and this compound does not show temperature dependence in the chemical shift. At first we could be tempted to relate the decrease of δ and the absence of temperature dependence with the absence of the double minimum. But in acetylacetone, where the double minimum is present, an increase of δ with temperature should be expected but a decrease is observed. So it is not quite clear how important the tunnelling mechanism is. For acetylacetone another type of enol-enol tautomerism was proposed[9] and in this case it was assumed that the enol tautomer was present in two different forms in rapid equilibrium. These two forms would be a symmetrical form, with the hydrogen atom at the same distance of both oxygen atoms and an asymmetric state with the hydrogen more localized in one of the -OH bonds. These states would correspond to different excitations of the donor-acceptor vibration levels. Because of the small difference in energy between these two states, they would both be populated at room temperature and would be in rapid equilibrium. With an increase of temperature, the donor-acceptor vibration levels would be excited, and more protons would be moving in an asymmetric potential, explaining that way the decrease of chemical shift with increased temperature. That could be the case for acetylacetone, but not for the hexafluor substituent.

The effects of β-substituents do not make the situation clearer.[10] Table I. shows some experimental results for symmetric and non-symmetric substituents. The only thing that is clear from these results is that the chemical shift varies in the same direction as the electron-donating ability of the substituent group. For symmetrical cases we will probably have a double minimum potential. On the other hand, for the case of $-CF_3$ and $-\phi$ groups, which differ strongly in their electronic

Table I
from ref. 10



No.	Substituent X	Substituent Y	δ^{exp}_{OH} (ppm)	$\delta^{calc.}_{OH}$ (ppm)	K (ppm)
(1)	—CF_3	—CH_3	14·24[a]	14·23	+0·01
(2)	—CF_3	—2-C_4H_3O	14·3[b]	14·26	+0·04
(3)	—CF_3	—2-C_4H_3Se	14·50[c]	14·48	+0·02
(4)	—CF_3	—2-C_4H_3S	14·64	14·58	+0·06
(5)	—CF_3	—C_6H_5	15·06	14·99	+0·07
(6)	—C_4F_9	—2-C_4H_3O	14·80[b]	14·79	+0·01
(7)	—C_4F_9	—2-C_4H_3S	15·10[b]	15·11	−0·01
(8)	—CH_3	—2,4,6-—$(CH_3)_3C_6H_2$	15·40[d]	15·48	−0·08
(9)	—CH_3	—2-C_4H_3Se	15·56	15·65	−0·09
(10)	—CH_3	—2-C_4H_3S	15·66[a]	15·75	−0·09
(11)	—CH_3	—3-C_4H_3Se	15·90	15·86	+0·04
(12)	—CH_3	—*p*-NO_2-C_6H_4	15·92	15·90	+0·02
(13)	—CH_3	—*t*-C_4H_9	15·95	15·95	0·00
(14)	—CH_3	—C_6H_5	16·11	16·16	−0·05
(15)	—2-C_4H_3O	—2-C_4H_3Se	15·61	15·68	−0·07
(16)	—2-C_4H_3O	—3-C_4H_3Se	15·80	15·89	−0·09
(17)	—2-C_4H_3O	—C_6H_5	16·3[b]	16·19	+0·11
(18)	—2,4,6-$(CH_3)_3C_6H_2$	—C_6H_5	16·3[d]	16·24	+0·06
(19)	—2-C_4H_3Se	—3-C_4H_3Se	16·10	16·11	−0·01
(20)	—2-C_4H_3Se	—C_6H_5	16·31	16·41	−0·10
(21)	—2-C_4H_3S	—3-C_4H_3Se	16·12	16·21	−0·09
(22)	—3-C_4H_3Se	—C_6H_5	16·63	16·62	+0·01
(23)	—*p*-NO_2-C_6H_4	—*t*-C_4H_9	16·4[d]	16·45	−0·05
(24)	—*p*-NO_2-C_6H_4	—C_6H_5	16·64	16·66	−0·02
(25)	—*t*-C_4H_9	—C_6H_5	16·7[d]	15·71	−0·01

and steric properties, we would expect a very deformed potential. However, the chemical shift for this compound is almost the same for acetylacetone.

It would be interesting to examine the behavior of these compounds in a situation where a possible tunnelling mechanism is absent or at least very ineffective. That would imply a low temperature study and in such condition these compounds will be in solid phase.

Solid state NMR has been used for many years as a tool for the study of solids. Chemical shifts are easily observed in liquid phase due to the fact that the much stronger dipole-dipole interaction is averaged to zero. But in solid state this is not the case and in general what is observed is a broad line, and small effects like chemical shifts cannot be measured.

Much effort has been made to develop techniques to try to average to zero the strong dipole-dipole interaction allowing the measurement of the chemical shift. Today multi-pulse techniques[11] can be used for this purpose and chemical shifts are being measured with high accuracy.[12] One of the great advantages of solid state NMR is the possibility of measuring the components of the tensor chemical shift, since in the liquid phase only the average chemical shift is measured. The components can be very useful in explaining directional properties of chemical bonds.

So we propose the utlization of high-resolution solid-state NMR techniques to investigate the hydrogen bond in these compounds.

For compounds in which we would expect a symmetrical or near symmetrical double minimum, an abrupt change in δ would indicate the importance of the tunnelling mechanism. In the case of the hexafluor acetylacetone we would expect no changes or very small changes, since we know a priori that the potential has no double minimum. Now, a large change in this case would indicate that another type of mechanism is operative here, which could be a thesis subject for someone else, starting with a more precise calculation of the potential.

REFERENCES

1. H. S. Jarrett, M. S. Sadler and J. N. Schoolery, J. Chem. Phys., 21, 2092 (1953).
2. L. W. Reeves, Can. J. Chem., 35, 1351 (1957).
3. Z. Yoshida, H. Ogoshi and T. Tokumitsu, Tetrahedron, 26, 5691 (1970).
4. S. Forsen and M. N. Nilsson, Arkiv. Kemi., 19, 569 (1963).
5. J. L. Burdett and M. T. Rogers, J. Amer. Chem. Soc., 86, 2105 (1964).
6. E. W. Garbish, J. Amer. Chem. Soc., 87, 505 (1965).
7. P. Schuster, Chem. Phys. Letters, 3, 433 (1969).
8. M. A. C. Nascimento and C. C. Neto, unpublished results.
9. P. K. K. Dea, Dissertation, California Institute of Technology, 1972.
10. N. N. Shpet'ko, Org. Mag. Res., 5, 215 (1973).
11. R. W. Vaughan in "Annual Reviews in Material Science", Vol. 4, edited by R. A. Huggins, R. H. Bube and R. W. Roberts, 1974, and references therein.
12. L. S. Schreiber and R. W. Vaughan, Chem. Phys. Letters, 28, 586 (1974).