

Modified Effective Potentials for Transition Metal Atoms

Thesis by

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## I. Introduction

Melius, Olafson and Goddard<sup>1</sup> have developed techniques for obtaining ab initio effective potentials to replace the core electrons of transition metals and still obtain ab initio quality descriptions of the valence electrons (4s, 4p and 3d). Using these ab initio effective potentials (AI-EP) in calculations of various electronic states of atoms and molecules leads to good agreement with the results of full-electron ab initio calculations. However, for transition metals such as Ni and Fe, even extensive ab initio calculations agree poorly with experimental results. For example, for Ni the separation of the  $^3D (s^1d^9)$  and  $^3F (s^2d^8)$  states should be 0.03 eV, whereas ab initio calculations using a large basis set yield a separation of -2.29 eV. The difficulty here seems to involve correlations among the d orbitals. To include such effects would require f basis functions (very expensive for molecules) and extensive configuration interaction.

In this paper, we propose an alternate approach in which the effective potential is modified to include in an average way these various correlation effects. The form of the modification is based on simple ideas concerning the role of such correlation effects and the magnitude of the modifications are determined so as to yield correct excitation energies and ionization potentials for the atom. In this paper we obtain modified effective potentials (MEP) for Ni and Fe, and they are tested by solving for the potential curves of several states of NiH and FeH.

## II. Modified Effective Potential

As mentioned above, the  ${}^3F(s^2d^8)$  state of Ni should be 0.03 eV<sup>3</sup> above the  ${}^3D(s^1d^9)$  state, whereas ab initio Hartree-Fock calculations<sup>4</sup> place the  ${}^3F$  state 2.29 eV below the  ${}^3D$  state. We believe that this is a result of the extra correlation error in the  ${}^3D$  state due to the additional doubly-occupied d orbital. Including these correlation effects will lead to a slight contraction of the d orbitals and a substantial decrease in the total energies of both states, but an appropriately larger decrease in favor of the  ${}^3D$  state. We include these correlation effects by adding an additional term,  $\bar{V}_d$ , to the d effective potential. In doing so we apply two restrictions:

- (a) Orbitals centered on atoms far from the Ni or Fe atom being considered should not be affected by the correlations in the d orbitals. Thus we require that

$$\int_0^\infty \bar{V}_d \rho(r) r^2 dr = 0$$

for  $\rho = \text{constant}$  and for  $\rho = |r|$ .

- (b) The new orbitals obtained using  $\bar{V}_d$  should be concentrated in the same region as the original ab initio orbitals (since the correlations lead to only a slight contraction of the d orbitals with little change in electron density).

Similar considerations apply to the 4s orbital. Even for the  $s^1d^9$  states there are considerable correlation corrections involving the 4s

orbitals. A simple way to think about this is to consider that an electron in the 4s orbital will polarize the core and thus decrease its energy. These effects are included in correlation terms such as 4s → 4p simultaneous with 3p → 3d and 4s → 4p simultaneous with 3d → 4f, but are excluded from Hartree-Fock calculations. We expect these correlation terms to result in only a small change in the shape of the 4s orbital and hence have applied restrictions (a) and (b) above to a modified s potential  $\bar{V}_{s-d}$  and a modified p potential  $\bar{V}_{p-d}$ .

Each correction term  $\bar{V}_\ell$  is given by

$$\bar{V}_\ell = C_\ell \left( \frac{1}{r^2} e^{-\alpha_\ell r^2} - \gamma_\ell e^{-\beta_\ell r^2} \right)$$

which is of the same form as the AI-EP:

$$V_\ell = \sum_k C_k r^{n_k} e^{-\zeta_k r^2}$$

Applying condition (a) above leads to

$$\gamma_\ell^2 = 4\beta_\ell^3/\alpha_\ell \quad \text{for } \rho = \text{constant}$$

$$\gamma_\ell = \beta_\ell^2/\alpha_\ell \quad \text{for } \rho = |\mathbf{r}|$$

or equivalently to

$$\alpha_\ell = \beta_\ell/4$$

$$\gamma_\ell = 4\beta_\ell$$

Condition (b) above was satisfied through the following procedure: a typical s or d orbital<sup>5</sup> ( $\psi^2 r^2$ ) was plotted against  $\bar{V}_{s-d}$  or  $\bar{V}_d$  over a range of  $\beta$ . As a starting point, we used the values of  $\beta_{s-d}$  and  $\beta_d$  for which the minimum of  $\bar{V}_\ell$  occurred at the maximum amplitude of the corresponding orbital. An SCF calculation was necessary to determine the final values, as the shapes of the orbitals proved to be very sensitive functions of  $\beta$ . We chose  $\beta_{p-d}$  to equal  $\beta_{s-d}$ . The final results are shown in Table I. The AI-EP and MEP orbitals are compared in Figures 1-4.

The values of  $C_\ell$  were then varied to yield the correct separations for the following key states of Ni and Fe, respectively: the lowest-lying  $s^2$  ( $^3F$  and  $^5D$ ),  $s^1$  ( $^3D$  and  $^5F$ ) and  $s^1 p^1$  ( $^5D$  and  $^7D$ ) states of the atom and the lowest-lying ionic state ( $^2D(s^0 d^8)$  and  $^6D(s^1 d^6)$ ). The optimum values are listed in Table I. The MEP's are tabulated in Table II, and  $\bar{V}_\ell$  is shown in relation to  $V_\ell$  (AI-MEP) and  $V_\ell$  (MEP) in Figures 5-10.

A guiding principle in this approach to modifying effective potentials is to obtain potentials that lead to orbital shapes consistent with those that would be obtained from accurate ab initio calculations. In this way we may expect that orbitals on different centers will overlap and interact correctly and hence lead to accurate bond energies, bond lengths and potential curves. Note that no molecular information is used in determining the effective potential.

### III. Basis Set Information

The basis sets are from those optimized by Wachters<sup>5</sup> for the ground states of the neutral atoms. We use all five d primitives, but the four tightest functions are contracted together with relative coefficients from Wachters' Hartree-Fock calculations. As discussed elsewhere,<sup>1</sup> only the outer four of Wachters' 4s functions are required for describing the coreless Hartree-Fock orbital of the AI-EP. The tightest two of these functions were contracted using relative coefficients from a Hartree-Fock calculation on the high spin state ( $s^1d^9$  for Ni and  $s^1d^7$  for Fe). We used four p basis functions with orbital exponents of 0.85 times the value of the corresponding s function. The tightest three p basis functions were contracted together based on the p orbital from the Ni  $s^1p^1d^8$  and Fe  $s^1p^1d^6$  high spin state.

For the calculations on NiH and FeH, the H basis consisted of four s functions (based on  $\delta = 1.0$ ) contracted to two, plus a p<sub>z</sub> basis function with orbital exponent 0.230. These basis sets are summarized in Table III.

## IV. Results

### A. Nickel

The nickel MEP was tested on various states of Ni, Ni<sup>+</sup> and Ni<sup>++</sup>. The highest spin state of the basic configurations ( $s^1d^9$ ,  $s^2d^8$ ,  $d^{10}$  and  $s^1p^1d^8$  for Ni;  $d^9$  and  $s^1d^8$  for Ni<sup>+</sup>;  $d^8$  for Ni<sup>++</sup>) were solved for at the Hartree-Fock level. The resulting  $\underline{s}$  and  $\underline{d}$  orbitals were then used as a basis for a complete (denoted hereinafter as GVB-CI) CI to obtain the higher states. These results are summarized in Table IV. The key states mentioned in Section II ( $^3F$ ,  $^3D$ ,  $^5D$ , and  $^2D$ ) are all within 0.04 eV of the experimental excitation energy. In every case, the CI calculations give correct orderings and reasonable separations for the excited states. The results are poorest for the  $^1S(d^{10})$  state, the excitation energy being over 3 eV too high (this is, however, about 4.5 eV better than the AI-EP results).

### B. Iron

Table V was prepared in a similar fashion for iron. The configurations used for Hartree-Fock calculations were  $s^2d^6$ ,  $s^1d^7$ ,  $s^1p^1d^6$  and  $d^8$  for Fe,  $s^1d^6$  and  $d^7$  for Fe<sup>+</sup>, and  $d^6$  for Fe<sup>++</sup>. The key states ( $^5D$ ,  $^5F$ ,  $^7D$  and  $^6D$ ) are fit within 0.03 eV. The  $^4F(d^7)$  state of Fe<sup>+</sup> was used as an additional test when determining  $C_{s-d}$  and  $C_d$ : this state was 0.53 eV too high, as it was not possible to fit both the  $^5D(s^1d^6)$  and  $^4F(d^7)$  states of the ion. This is probably due to the large differences at the AI-EP level (the  $^5D$  state is 2.04 eV too low whereas the  $^4F$  state is high by only 0.45 eV). These states required greatly

different degrees of modification to obtain an accurate description. The CI calculation lowered the  $^4F$  state by 0.15 eV.

As with nickel, the  $s^0$  state of the atom is almost 4 eV too high using the MEP, but about 3.5 eV better than with the AI-EP. The CI results are generally good, but there are some incorrect orderings of states for  $Fe^+$  and  $Fe^{++}$ . These are, though, small and occur in CIs of lower spin than that of the corresponding Hartree-Fock calculation (the nickel CIs were of the same spin).

### C. NiH

We carried out calculations on NiH to determine the accuracy of the MEP in describing the interaction of Ni with another atom. In order to correctly describe dissociation of the molecule, we correlated the orbitals forming the NiH bond (a GVB(1) calculation).<sup>6</sup> The energies for various internuclear distances are listed in Table VI. These points were fit with a cubic spline curve (Figure 11) and the results are summarized in Table VII. The agreement is quite good: for the  $^2\Delta$  state, the experimental values<sup>7</sup> are  $R_e = 2.79$  b and  $\omega \sim 2000$   $cm^{-1}$ , whereas we obtain 2.74 b and 1911  $cm^{-1}$ . The bond energy of this state is not well known, but Gaydon<sup>8</sup> gives  $2.6 \pm 0.3$  eV and we obtained 2.88 eV. The GVB orbitals are plotted in Figure 12.

### D. FeH

We calculated potential curves for the  $^4\Delta$  and  $^4\Pi$  states of FeH, each of which involve basically an Fe  $s^1d^7$  configuration for small R. At large R, there are difficulties in solving for these states since the Fe  $s^2d^6$  state is 0.87 eV lower at  $R = \infty$  and also leads to  $^4\Delta$  and  $^4\Pi$  states.



Thus for  $R > 4.0$  b, we solved for the  ${}^6\Delta$  states using an Fe  $s^1d^7$  configuration.<sup>9</sup> The potential curves are based on GVB-CI's using the  $\underline{s}$  and  $\underline{d}$  orbitals from the SCF calculation [GVB(1) quartet for  $R \leq 4.0$  b and Hartree-Fock sextet for  $R > 4.0$  b]. The points used for the cubic spline fit (Figure 13) are given in Table VIII. The spectroscopic data are summarized in Table IX, and the GVB orbitals are shown in Figure 14.

Table I. The parameters of the correlation term,  $\bar{V}_\ell$ , for the MEP

$$\left( \bar{V}_\ell = C_\ell \left( \frac{1}{r^2} e^{-\alpha_\ell r^2} - \gamma_\ell e^{-\beta_\ell r^2} \right) \right) .$$

	Ni	Fe
$\beta_{s-d}$	0.15	0.12
$\beta_{p-d}$	0.15	0.12
$\beta_d$	2.0	1.5
$C_{s-d}$	1.50	2.05
$C_{p-d}$	0.50	0.60
$C_d$	0.85	0.87

Table II. The total MEP for Ni and Fe ( $V_l = \sum_k C_k r^{n_k} e^{-\zeta_k r^2}$ )

	n	Ni		Fe	
		$\zeta$	C	$\zeta$	C
$V_{s-d}$	-2	0.959	7.465	0.980	7.968
	0	0.504	0.848	0.499	1.290
	0	8.87	-28.67	9.44	-51.14
	-2	0.0375	1.50	0.03	2.05
	0	0.15	- 0.90	0.12	- 9.84
	-2	0.50	- 0.85	0.375	- 0.87
	0	2.00	6.80	1.50	5.22
$V_{p-d}$	-2	0.465	4.807	0.388	4.457
	0	5.02	23.61	5.97	31.08
	-2	0.0375	0.50	0.03	0.60
	0	0.15	- 0.30	0.12	- 2.88
	-2	0.50	- 0.85	0.375	- 0.87
	0	2.0	6.80	1.50	5.22
$V_d$	-1	21.66	- 9.827	19.88	- 9.925
	-1	0.659	- 1.247	0.591	- 1.380
	0	5.02	-12.84	4.52	-12.66
	-2	0.50	0.85	0.375	0.87
	0	2.00	- 6.80	1.50	- 5.22

Table III. Basis set summary.

	Ni		Fe		H	
	$\zeta$	C	$\zeta$	C	$\zeta$	C
s	2.39417	-0.01060	2.01847	-0.01462	13.362	0.01906
	0.918169	-0.12519	0.779935	-0.13323	2.013	0.13424
	0.130176	- - -	0.114220	- - -	0.454	0.47449
	0.046392	- - -	0.041889	- - -	0.123	- - -
p	2.03504	-0.02586	1.71570	-0.03653	0.230 <sup>a</sup>	- - -
	0.780444	0.03847	0.662945	0.07605	- - -	- - -
	0.110650	0.62107	0.097087	0.69593	- - -	- - -
	0.039433	- - -	0.035606	- - -	- - -	- - -
d	48.9403	0.02706	41.4526	0.02511	- - -	- - -
	13.7169	0.14598	11.5403	0.13626	- - -	- - -
	4.63951	0.36418	3.88543	0.35323	- - -	- - -
	1.57433	0.46438	1.32380	0.46867	- - -	- - -
	0.486409	- - -	0.416680	- - -	- - -	- - -

<sup>a</sup><sub>p<sub>z</sub></sub> only

Table IV. Energy comparisons for various states of Ni, Ni<sup>+</sup> and Ni<sup>++</sup> (all energies are in eV).

State	Experi- ment	AI-EP Hartree- Fock	Hartree- Fock	Modified Effective Potential						
				GVB-CI <sup>c</sup>						
				<sup>3</sup> D(s <sup>1</sup> d <sup>8</sup> )	<sup>3</sup> F(s <sup>2</sup> d <sup>8</sup> )	<sup>1</sup> S(d <sup>10</sup> ) <sup>d</sup>	<sup>5</sup> D(s <sup>1</sup> p <sup>1</sup> d <sup>6</sup> ) <sup>e</sup>	<sup>2</sup> D(d <sup>9</sup> ) <sup>f</sup>	<sup>4</sup> F(s <sup>1</sup> d <sup>8</sup> )	<sup>3</sup> F(d <sup>8</sup> ) <sup>g</sup>
<sup>3</sup> D(s <sup>1</sup> d <sup>8</sup> )	0	2.29	0 <sup>b</sup>	0	0	0	0	0	0	0
<sup>3</sup> F(s <sup>2</sup> d <sup>8</sup> )	0.03	0 <sup>a</sup>	0.03		0.03					
<sup>1</sup> D(s <sup>1</sup> d <sup>8</sup> )	0.33			0.31						
<sup>1</sup> D(s <sup>2</sup> d <sup>8</sup> )	1.59				1.66					
<sup>1</sup> S(d <sup>10</sup> )	1.74	9.58	5.14			4.99				
<sup>3</sup> P(s <sup>2</sup> d <sup>8</sup> )	1.86				2.52					
<sup>1</sup> G(s <sup>2</sup> d <sup>8</sup> )	2.65				3.23					
<sup>5</sup> D(s <sup>1</sup> p <sup>1</sup> d <sup>8</sup> )	3.22	1.93	3.18				3.05			
<sup>5</sup> G(s <sup>1</sup> p <sup>1</sup> d <sup>8</sup> )	3.37						3.14			
<sup>5</sup> F(s <sup>1</sup> p <sup>1</sup> d <sup>8</sup> )	3.55						3.31			
<sup>1</sup> S(s <sup>2</sup> d <sup>8</sup> )	- -				7.84					
<sup>5</sup> P(s <sup>1</sup> p <sup>1</sup> d <sup>8</sup> )	- -						5.36			
<sup>5</sup> D(s <sup>1</sup> p <sup>1</sup> d <sup>8</sup> )	- -						5.74			
<sup>5</sup> S(s <sup>1</sup> p <sup>1</sup> d <sup>8</sup> )	- -						6.19			
<sup>2</sup> D(d <sup>9</sup> )	7.62	8.26	7.60					7.53		
<sup>4</sup> F(s <sup>1</sup> d <sup>8</sup> )	8.70	6.70	8.46						8.46	
<sup>4</sup> P(s <sup>1</sup> d <sup>8</sup> )	10.63								10.94	
<sup>3</sup> F(d <sup>8</sup> )	18.20	22.86	26.45							26.41
<sup>3</sup> P(d <sup>8</sup> )	20.16									28.80

<sup>a</sup>E = -39.1170 h.

<sup>b</sup>E = -40.4943 h.

<sup>c</sup>The Hartree-Fock orbitals from the state at the head of a column are used in a GVB-CI to obtain all the states of that column. The energies are relative to the <sup>3</sup>D(s<sup>1</sup>d<sup>8</sup>) CI energy of -40.4943 h.

<sup>d</sup>s orbital from <sup>3</sup>D(s<sup>1</sup>d<sup>8</sup>) Hartree-Fock calculation, p orbitals from <sup>5</sup>D(s<sup>1</sup>p<sup>1</sup>d<sup>8</sup>) Hartree-Fock calculation,

<sup>e</sup>The configuration used at the Hartree-Fock level (d<sub>x<sup>2</sup>-y<sup>2</sup></sub><sup>1</sup> d<sub>z<sup>2</sup></sub><sup>1</sup> d<sub>xy</sub><sup>2</sup> d<sub>xz</sub><sup>2</sup> d<sub>yz</sub><sup>2</sup>) was not of pure D symmetry, and hence there is a CI energy lowering due to contributions from similar configurations.

<sup>f</sup>s orbital from <sup>3</sup>D(s<sup>1</sup>d<sup>8</sup>) Hartree-Fock calculation

<sup>g</sup>s orbital from <sup>4</sup>F(s<sup>1</sup>d<sup>8</sup>) Hartree-Fock calculation.

Table V. Energy comparisons for various states of Fe, Fe<sup>+</sup>, Fe<sup>2+</sup> (all energies are in eV).

State	Experiment	AI-EP Hartree- Fock	Hartree- Fock	Modified Effective Potential						
				GVB-CI <sup>c</sup>						
				<sup>5</sup> D(s <sup>2</sup> d <sup>6</sup> )	<sup>5</sup> F(s <sup>1</sup> d <sup>7</sup> )	<sup>3</sup> F(d <sup>8</sup> ) <sup>d</sup>	<sup>7</sup> D(s <sup>1</sup> p <sup>1</sup> d <sup>6</sup> )	<sup>6</sup> D(s <sup>1</sup> d <sup>6</sup> )	<sup>4</sup> F(d <sup>7</sup> ) <sup>e</sup>	<sup>5</sup> D(d <sup>6</sup> ) <sup>f</sup>
<sup>5</sup> D(s <sup>2</sup> d <sup>6</sup> )	0	0 <sup>a</sup>	0 <sup>b</sup>	0	0	0	0	0	0	0
<sup>5</sup> F(s <sup>1</sup> d <sup>7</sup> )	0.87	2.72	0.90		0.90					
<sup>3</sup> F(s <sup>1</sup> d <sup>7</sup> )	1.49				1.86					
<sup>5</sup> P(s <sup>1</sup> d <sup>7</sup> )	2.14				2.92					
<sup>3</sup> P(s <sup>2</sup> d <sup>6</sup> )	2.30			2.70						
<sup>7</sup> D(s <sup>1</sup> p <sup>1</sup> d <sup>6</sup> )	2.38	1.04	2.38				---	<sup>g</sup>		
<sup>3</sup> H(s <sup>2</sup> d <sup>6</sup> )	2.38			2.74						
<sup>3</sup> F(s <sup>2</sup> d <sup>6</sup> )	2.53			2.90						
<sup>3</sup> G(s <sup>1</sup> d <sup>7</sup> )	2.67				3.06					
<sup>3</sup> G(s <sup>2</sup> d <sup>6</sup> )	2.93			3.39						
<sup>5</sup> D(s <sup>1</sup> p <sup>1</sup> d <sup>6</sup> )	3.19							3.52		
<sup>5</sup> F(s <sup>1</sup> p <sup>1</sup> d <sup>6</sup> )	3.32							3.57		
<sup>3</sup> F(d <sup>8</sup> )	4.07	11.40	7.96			6.70				
<sup>6</sup> D(s <sup>1</sup> d <sup>6</sup> )	7.90	5.86	7.87					7.87		
<sup>4</sup> F(d <sup>7</sup> )	8.15	8.59	8.68						8.53	
<sup>4</sup> D(s <sup>1</sup> d <sup>6</sup> )	8.88							9.64		
<sup>4</sup> P(d <sup>7</sup> )	9.54								12.27	
<sup>2</sup> G(d <sup>7</sup> )	9.84								10.43	
<sup>2</sup> P(d <sup>7</sup> )	10.15								10.99	
<sup>2</sup> H(d <sup>7</sup> )	10.40								11.23	
<sup>2</sup> D(d <sup>7</sup> )	10.43								11.04	
<sup>4</sup> P(s <sup>1</sup> d <sup>6</sup> )	10.50							10.73		
<sup>4</sup> H(s <sup>1</sup> d <sup>6</sup> )	10.51							11.00		
<sup>5</sup> D(d <sup>6</sup> )	24.08	21.44	25.37							25.37
<sup>3</sup> P(d <sup>6</sup> )	26.51									28.46
<sup>3</sup> H(d <sup>6</sup> )	26.54									28.17
<sup>3</sup> F(d <sup>6</sup> )	26.71									28.55
<sup>3</sup> G(d <sup>6</sup> )	27.11									28.84

<sup>a</sup>E = -21.5558 h.

<sup>b</sup>E = -22.2480 h.

<sup>c</sup>The Hartree-Fock orbitals from the state of the head of a column are used in a GVB-CI to obtain all the states of that column. The energies are relative to the <sup>5</sup>D(s<sup>1</sup>d<sup>6</sup>) CI energy of -22.2480 h.

<sup>d</sup>s orbital from <sup>5</sup>D(s<sup>2</sup>d<sup>6</sup>) Hartree-Fock calculation.

<sup>e</sup>s orbital from <sup>6</sup>D(s<sup>1</sup>d<sup>6</sup>) Hartree-Fock calculation.

<sup>f</sup>s orbital from <sup>5</sup>D(s<sup>2</sup>d<sup>6</sup>) Hartree-Fock calculation.

<sup>g</sup>CI program does not calculate septet states.

Table VI. Energies for NiH from GVB(1) calculations using the MEP (energies are in Hartrees).

Internuclear Distance (Bohr)	$^2\Delta$	$^2\Pi$	$^2\Sigma^+$
1.25	-40.4168	-40.3315	-40.3903
2.00	-41.0286	-40.9892	-40.9756
2.25	-41.0742	-41.0457	-41.0363
2.50	-41.0942	-41.0742	-41.0675
2.75	-41.0993	-41.0854	-41.0808
3.00	-41.0957	-41.0859	-41.0828
4.00	-41.0515	-41.0486	-41.0478
5.00	-41.0146	-41.0133	-41.0129
6.00	-40.9974	-40.9966	-40.9970
$\infty$	-40.9936	-40.9936	-40.9936

Table VII. Summary of the spectroscopic parameters for NiH. Experimental values are included in parentheses.

State	$R_e(b)$	$E_e(b)$	Vertical Transition (eV)	Adiabatic Transition (eV)	$\omega$ (cm <sup>-1</sup> )	Bond Energy (eV)	Charge Transfer <sup>a</sup> to H	Mulliken Population of Ni 4s Orbital <sup>a</sup>
<sup>2</sup> $\Delta$	2.74	-41.0993	0	0	1911	2.88	0.1212	0.9472
	(2.79)				(2000)	(2.6 ± 0.3)		
<sup>2</sup> $\Pi$	2.88	-41.0866	0.38	0.35	1807	2.53	0.1710	0.8408
	2.93	-41.0831	0.50	0.44	1759	2.43	0.2540	0.6893

<sup>a</sup> R = 2.75 b.



**Table VIII. Energies for FeH from Hartree-Fock, GVB(1), and CI calculations using the MEP (energies are in hartrees).**

Inter-nuclear Distance (Bohr)	${}^6\Delta$		${}^4\Delta$		${}^4\Pi$	
	Hartree-Fock	GVB-CI <sup>a</sup> ( ${}^6\Delta$ orbs)	GVB(1)	GVB-CI <sup>b</sup> ( ${}^4\Delta$ orbs)	GVB(1)	GVB-CI <sup>b</sup> ( ${}^4\Pi$ orbs)
1.00			-21.3267	--	-21.3869	-21.3925
2.00			-22.7205	-22.7247	-22.7237	-22.7365
2.25			-22.7742	-22.7797	-22.7695	-22.7851
2.50			-22.8010	-22.8069	-22.7897	-22.8078
2.75			-22.8115	-22.8161	-22.7941	-22.8145
3.00			-22.8124	-22.8159	-22.7890	-22.8117
3.25			-22.8063	-22.8099	-22.7789	-22.8052
3.50			-22.7972	-22.8001	-22.7663	-22.7954
4.00			-22.7731	-22.7764		
4.50	-22.7108	-22.7417	-22.7243			
5.00	-22.7117	-22.7303	-22.6961			
5.50	-22.7125	-22.7231	-22.6710			
6.00	-22.7129	-22.7187	-22.7103			
6.50	-22.7132	-22.7163	-22.7012			
7.00	-22.7134	-22.7151	-22.7016			
7.50	-22.7137	-22.7146	-22.7012			

<sup>a</sup> The sextet Hartree-Fock orbitals were used as the basis for the CI.

<sup>b</sup> The quartet GVB(1) orbitals were used as the basis for the CI.

Table IX. Summary of spectroscopic parameters for FeH.

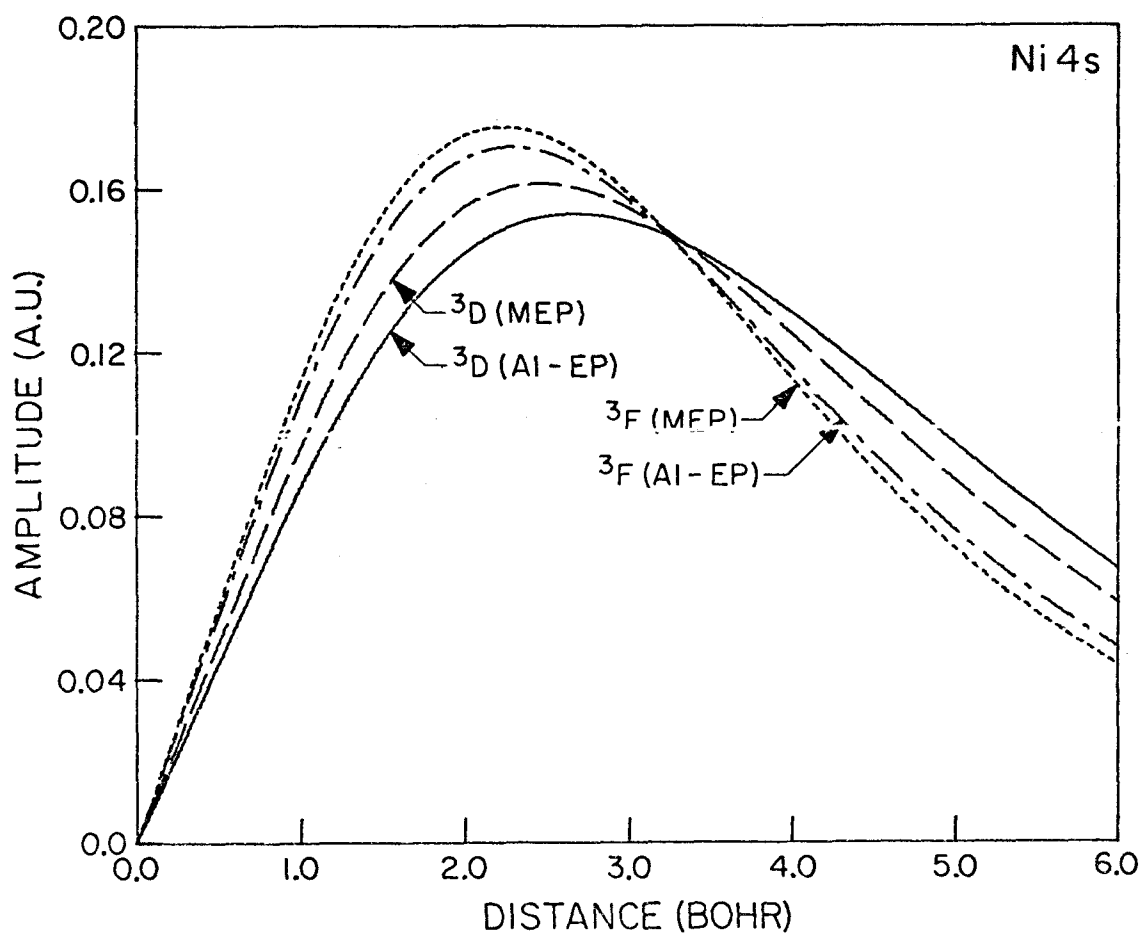
State	$R_e$ (b)	$E_e$ (b)	Vertical Transition (eV)	Adiabatic Transition (eV)	$\omega$ ( $\text{cm}^{-1}$ )	Bond Energy (eV)	Charge Transfer to H <sup>a</sup>	Mulliken Population of Fe 4s orbital <sup>a</sup>
$^4\Delta$	2.86	-22.8169	0	0	1741	2.79	0.0966	1.0524
$^4\Pi$	2.77	-22.8145	0.09	0.07	1924	2.73	0.0539	1.3086

<sup>a</sup>  $R = 2.75$  b.

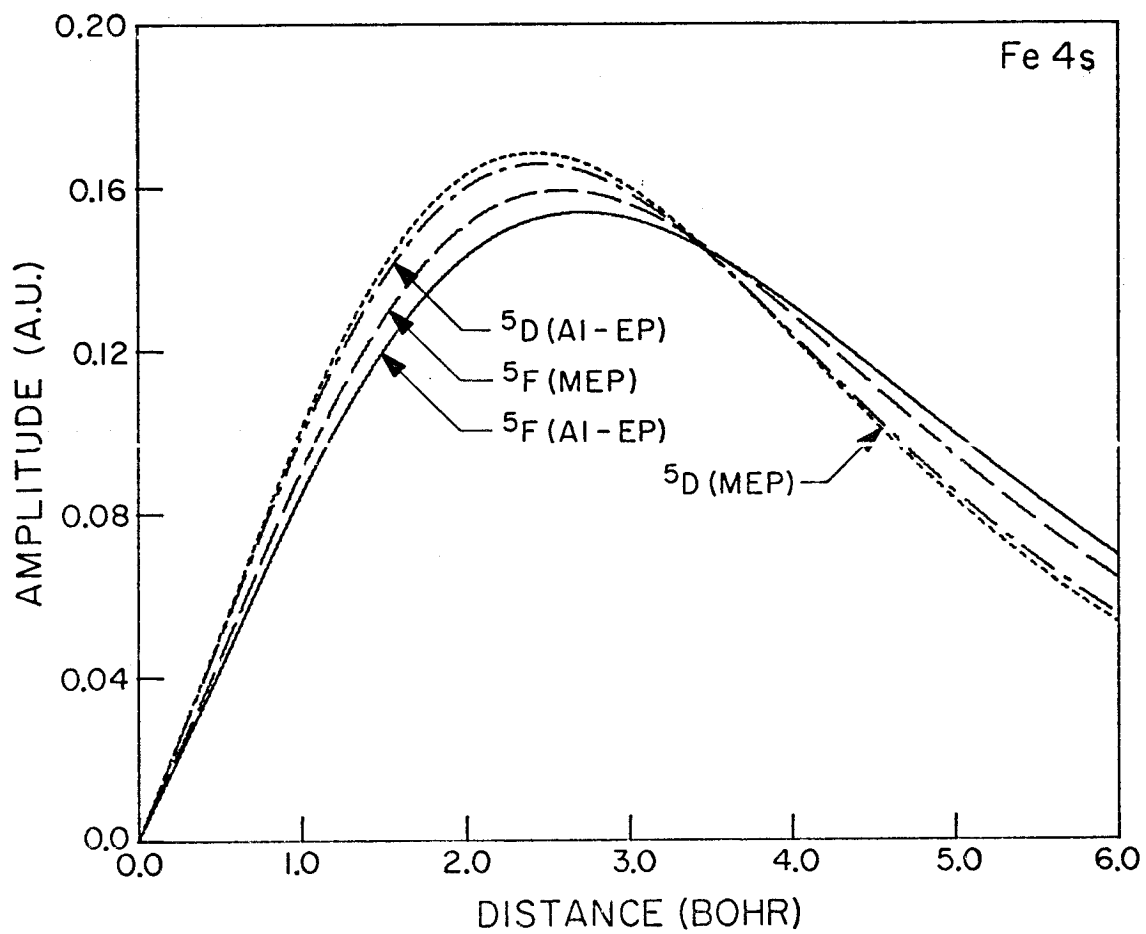
## References

1. C. F. Melius, B. D. Olafson, and W. A. Goddard III, Chem. Phys. Lett., 28, 457 (1974); see also C. F. Melius and W. A. Goddard III, Phys. Rev. A, 10, 1528 (1974).
2. C. E. Moore, Atomic Energy Levels, Vol. II, National Bureau of Standards (1952).
3. All experimental excitation energies referred to in this paper are a weighted average over the J levels of the state of spectral L and S (we do not include spin-orbit interaction in our calculations). The values are from C. Moore.<sup>2</sup>
4. For these states, it suffices to do only a Hartree-Fock calculation since they are pure states; thus a CI using the Hartree-Fock s and d orbitals would yield the same energy.
5. A. J. H. Wachters, J. Chem. Phys., 52, 1033 (1970).
6. W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Accts. Chem. Res., 6, 368 (1973).
7. B. Rosen, Spectroscopic Data Relative to Diatomic Molecules, Pergamon Press (1970).
8. A. G. Gaydon, Dissociation Energies and Spectra of Diatomic Molecules, Chapman and Hall (1968).
9. The lowest  ${}^6\Delta$  is also an  $s^2d^6$  configuration, but the trial orbitals used in the Hartree-Fock calculation were from the  $s^1d^7$  atomic states. The  $4s-3d_{z^2}$  rotations were not allowed and thus we obtained a good energy for the  $s^1d^7 {}^6\Delta$  state.
10. The  ${}^4\Delta$  curve between 4.5 and 5.5 b is hand-drawn.

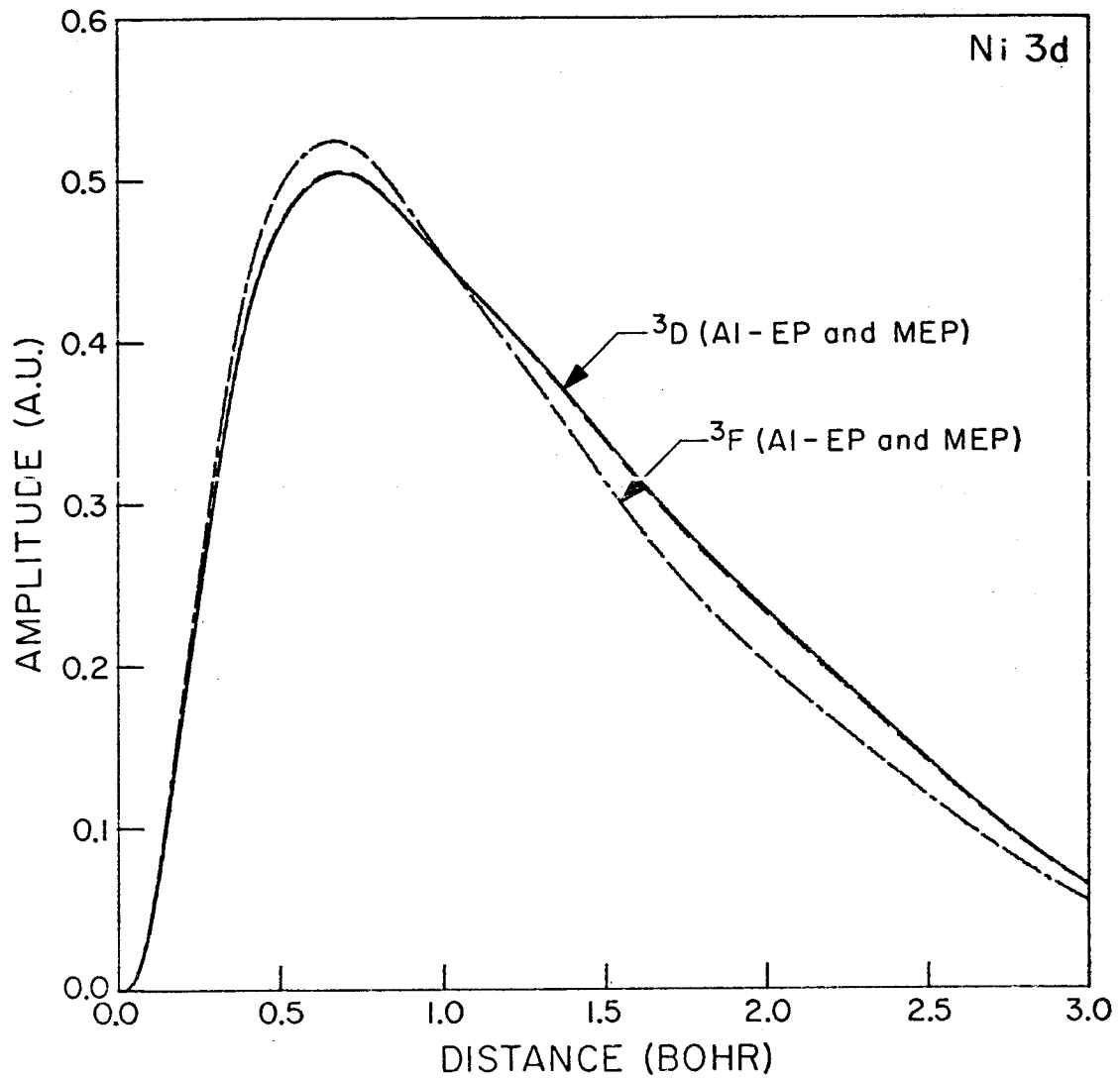
1. The 4s orbitals of Ni using the ab initio effective potential (AI-EP) and the modified effective potential (MEP) for the  ${}^3F(s^2d^8)$  and  ${}^3D(s^1d^9)$  states.



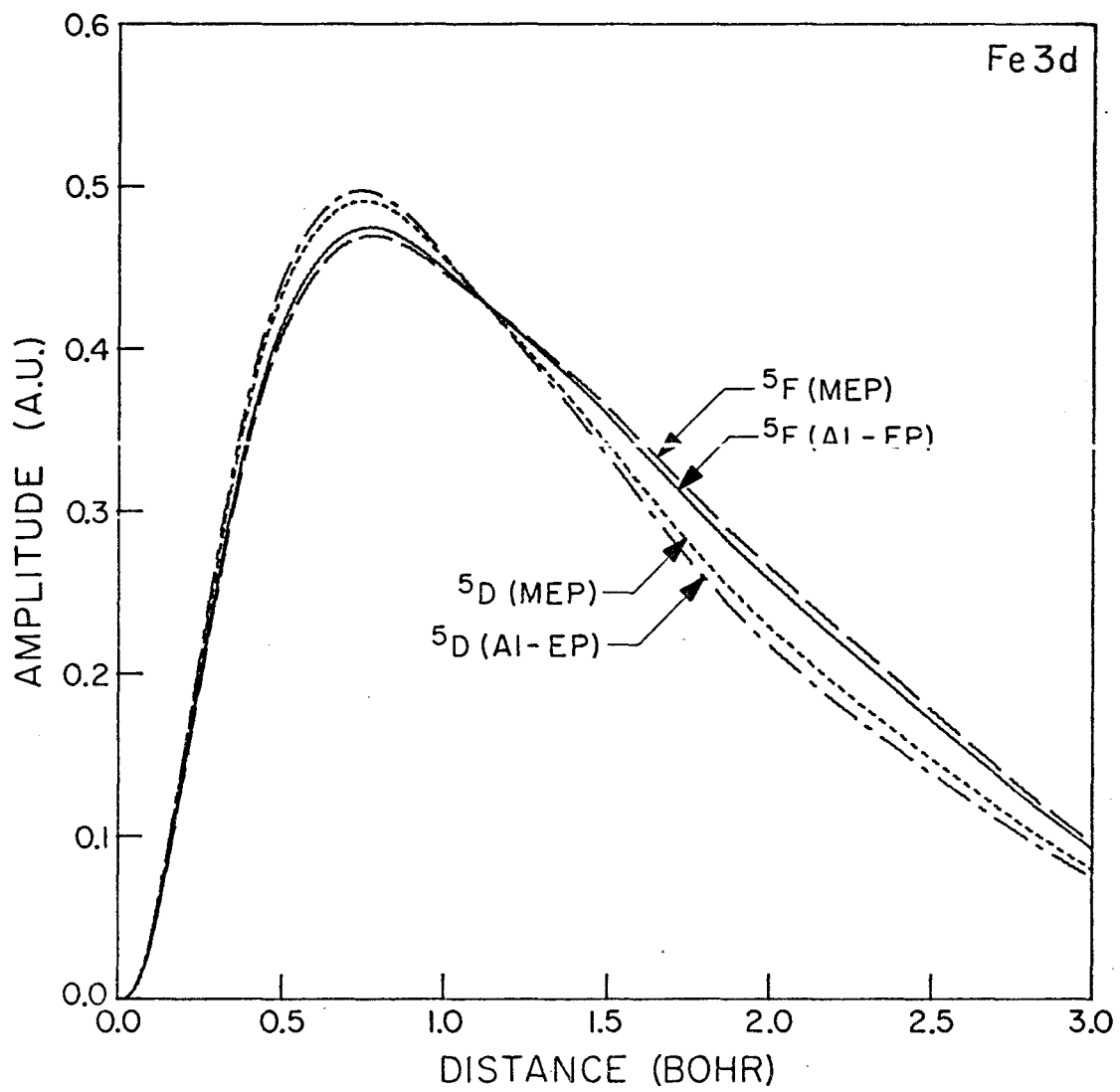
2. The 4s orbitals of Fe using the AI-EP and the MEP for the  $^5D(s^2d^6)$  and  $^5F(s^1d^7)$  states.



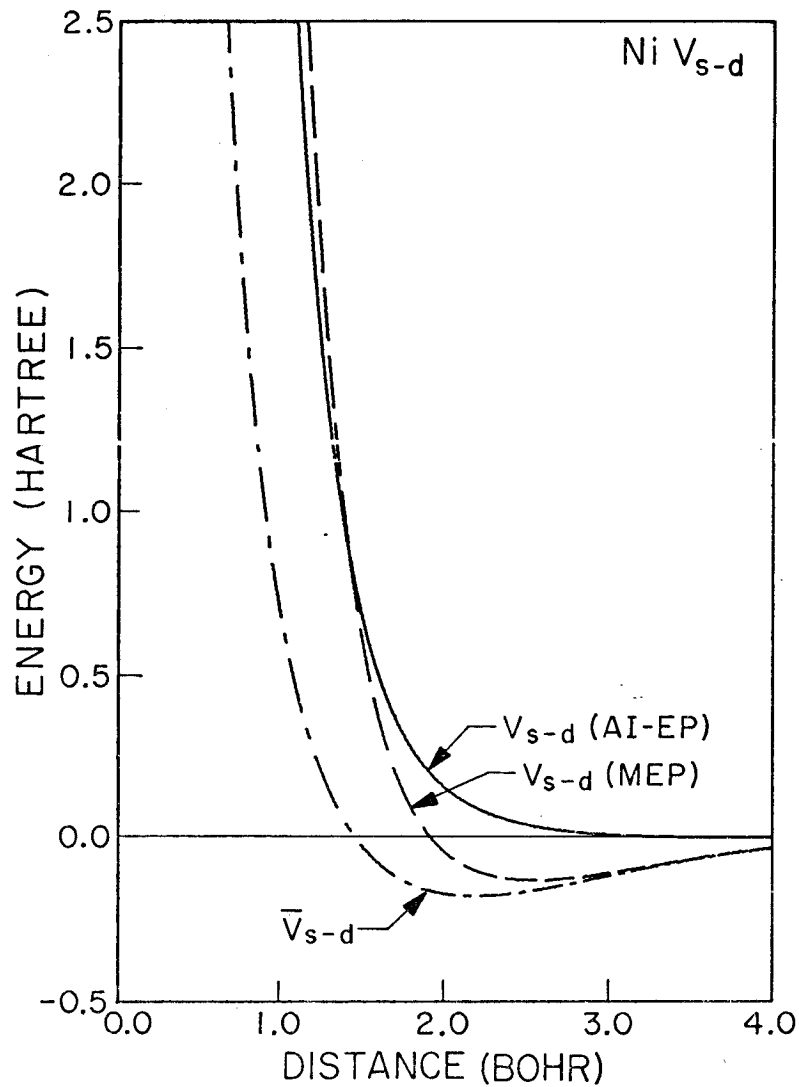
3. The 3d orbitals of Ni using the AI-EP and the MEP for the  ${}^3F(s^2d^8)$  and  ${}^3D(s^1d^9)$  states. The AI-EP and MEP orbitals are barely distinguishable.



4. The 3d orbitals of Fe using the AI-EP and the MEP for the  $^5D(s^2d^6)$  and  $^5F(s^1d^7)$  states.

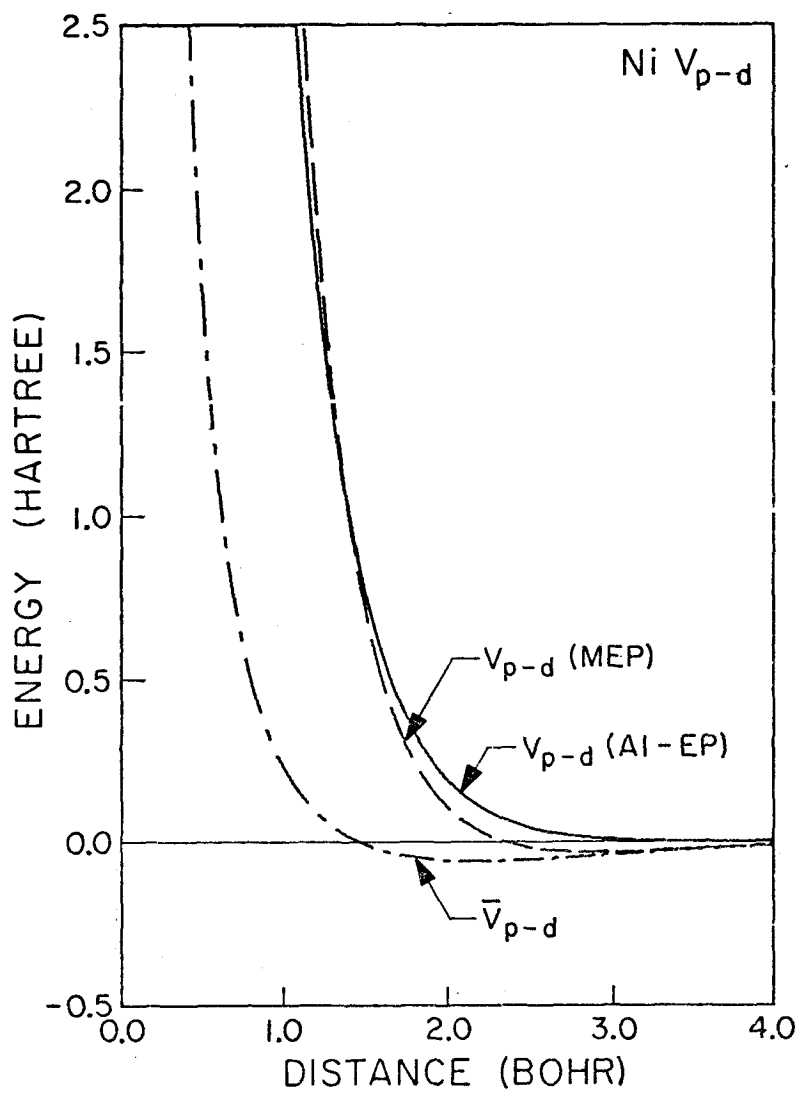


5. The s-d effective potential of Ni.  $\bar{V}_{s-d}$  is the modification which is added to the AI-EP, but note that  $\bar{V}_{s-d} + V_{s-d}(\text{AI-EP}) \neq V_{s-d}(\text{MEP})$ . This is because the term added to the d potential ( $\bar{V}_d$ ) must also be subtracted from the s-d potential:  $\bar{V}_{s-d} + V_{s-d}(\text{AI-EP}) - \bar{V}_d = V_{s-d}(\text{MEP})$ .

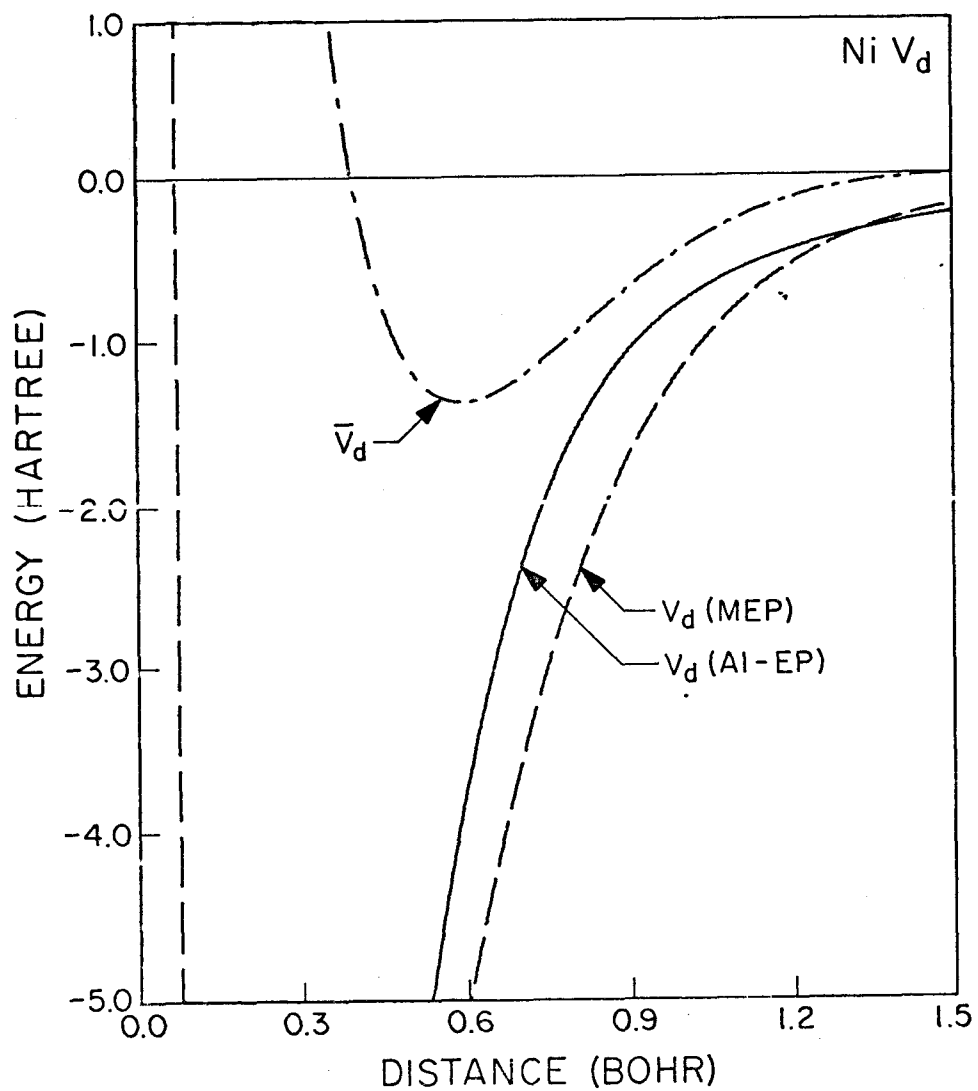




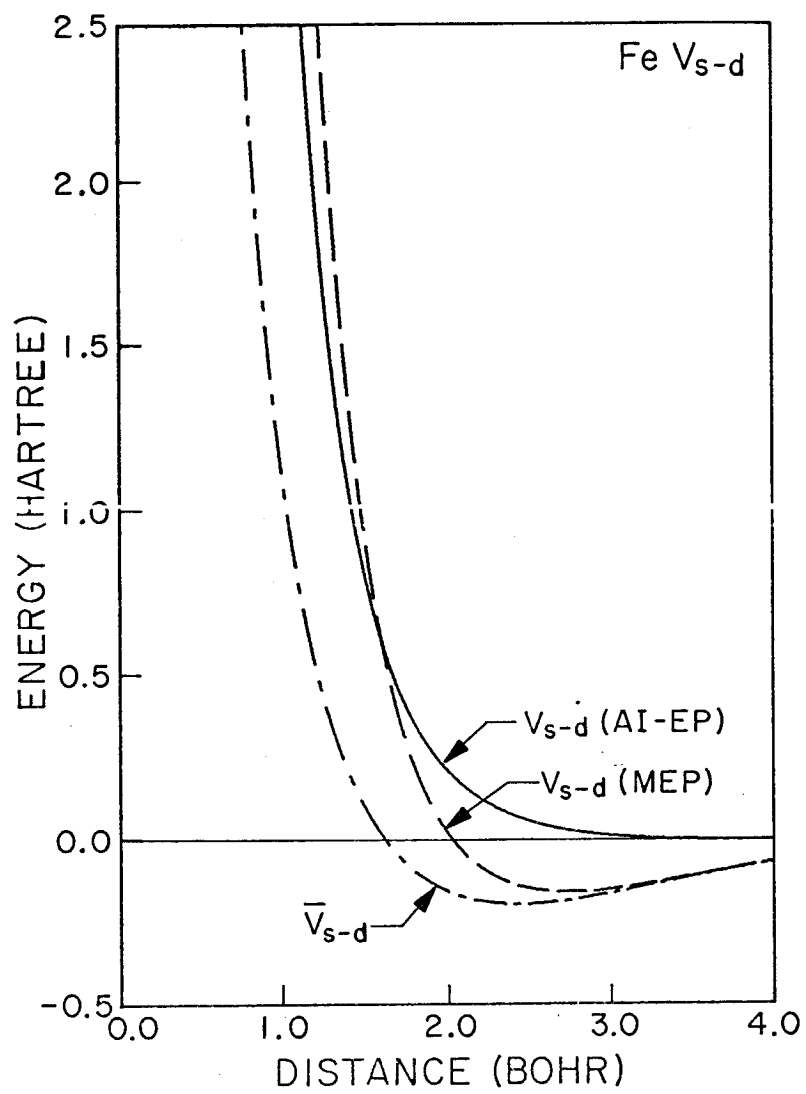
6. The p-d effective potential of Ni.  $\bar{V}_{p-d}$  is the modification which is added to the AI-EP, but again note that  $\bar{V}_{p-d} + V_{p-d}(\text{AI-EP}) \neq V_{p-d}(\text{MEP})$ . The explanation is analogous to that of Figure 5.



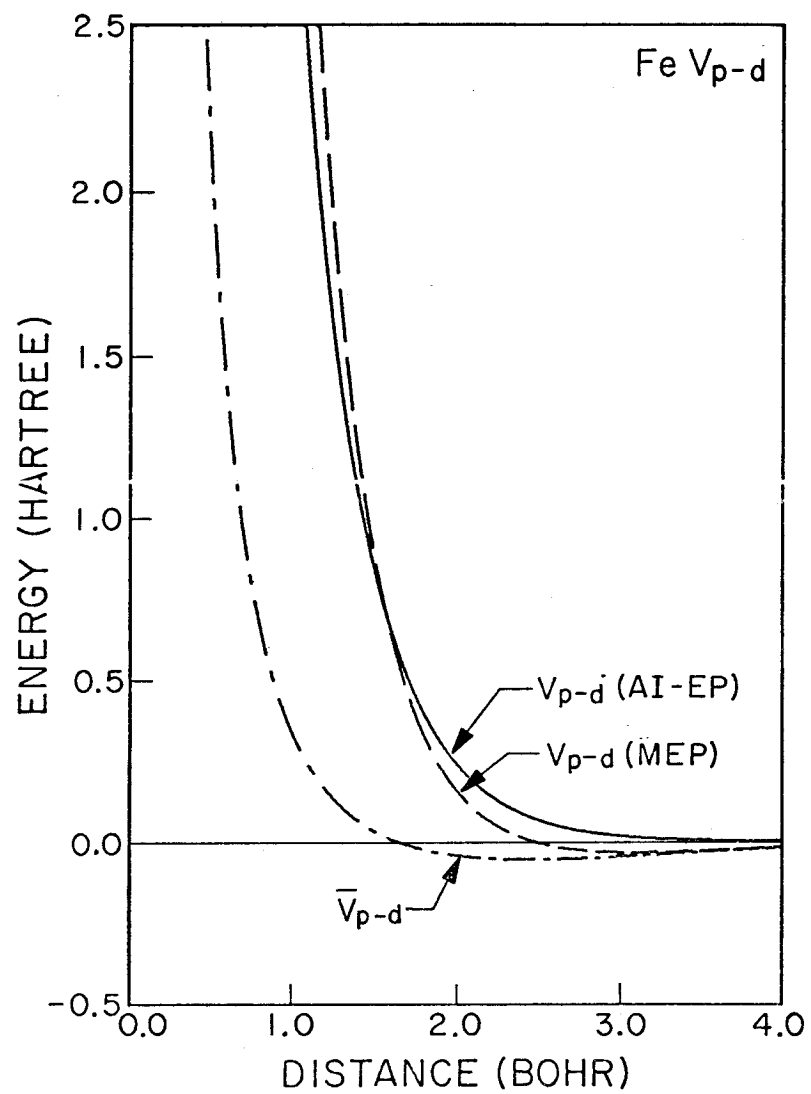
7. The d effective potential of Ni.  $\bar{V}_d$  is the modification which is added to the AI-EP:  $\bar{V}_d + V_d(\text{AI-EP}) = V_d(\text{MEP})$ .



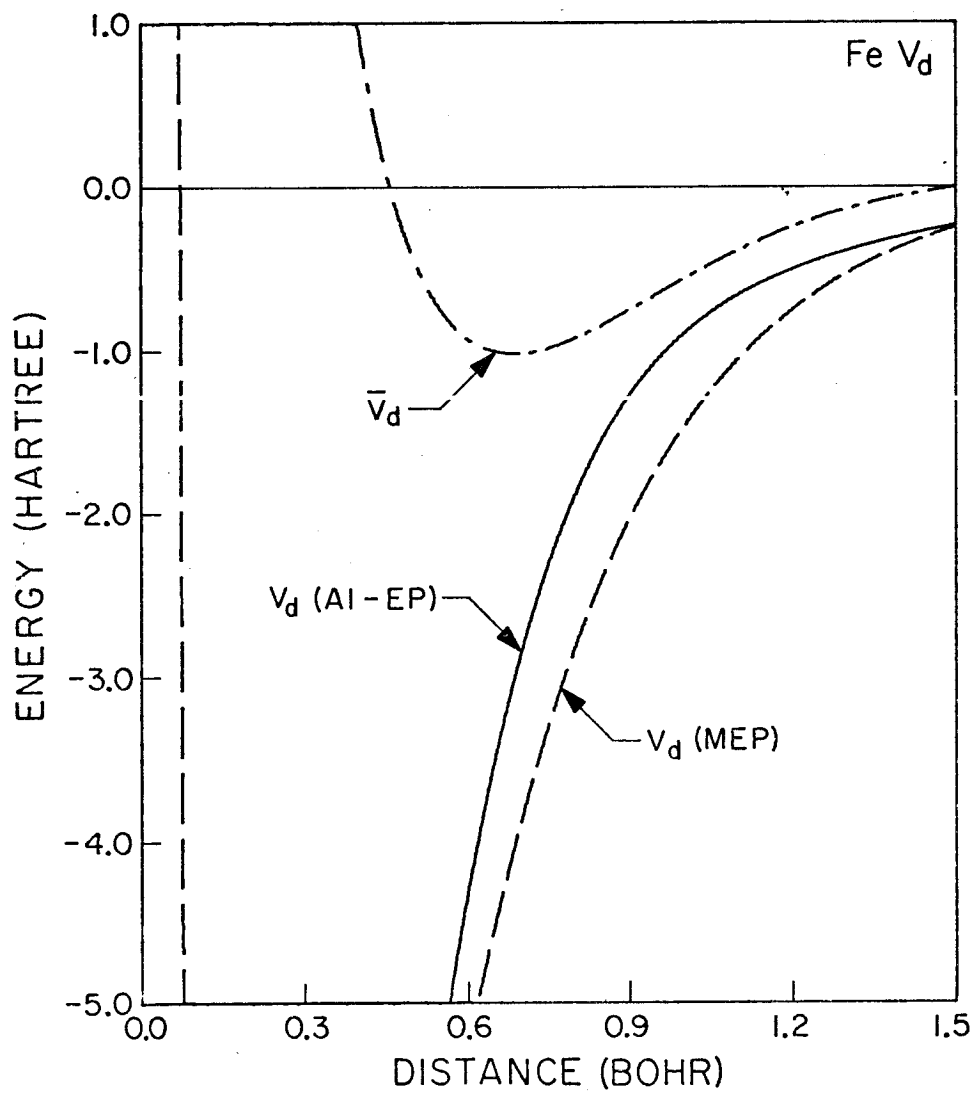
8. The s-d effective potential of Fe. See Figure 5 for explanation.



9. The p-d effective potential of Fe. See Figure 6 for explanation.

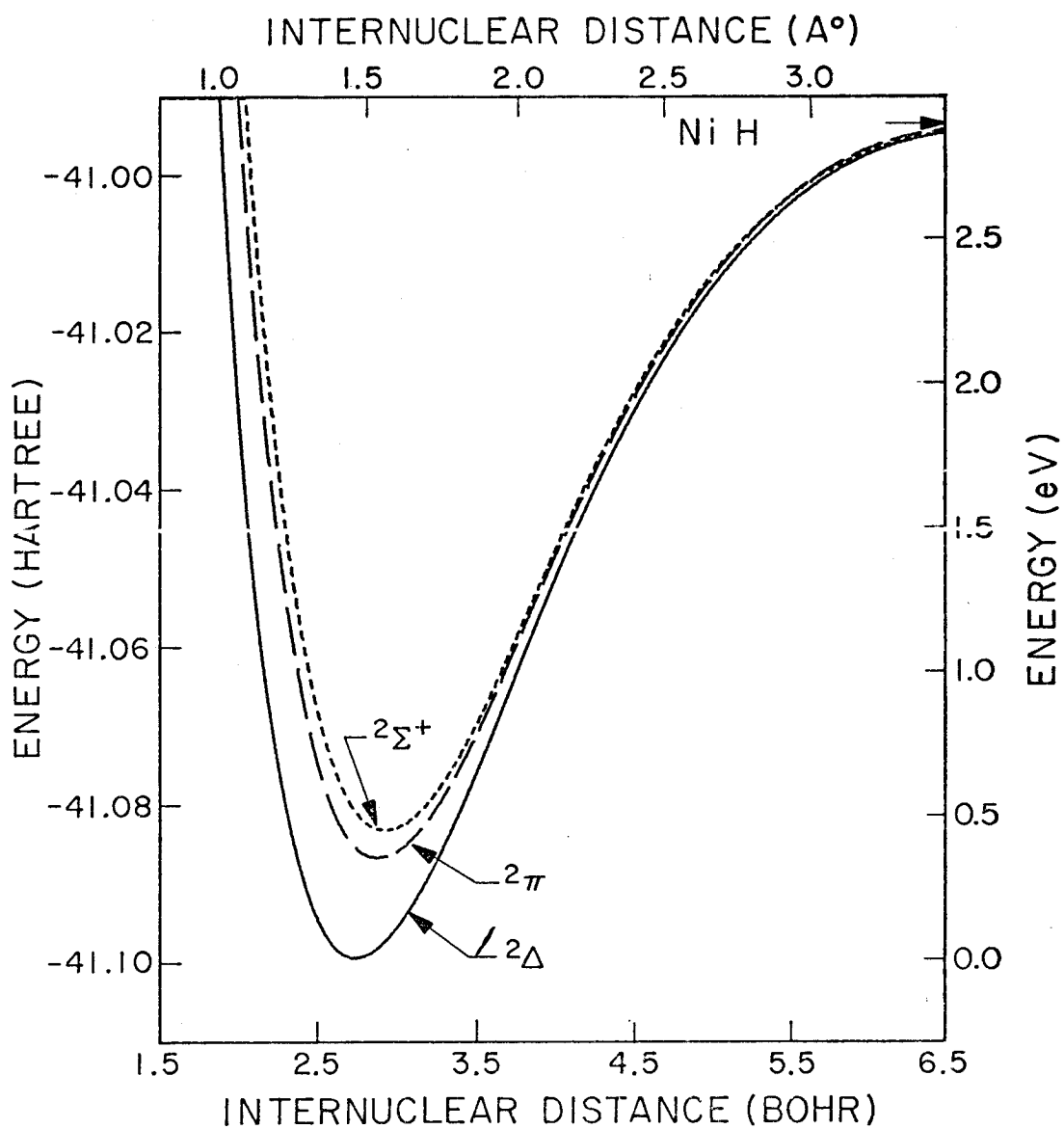


10. The d effective potential of Fe. See Figure 7 for explanation.

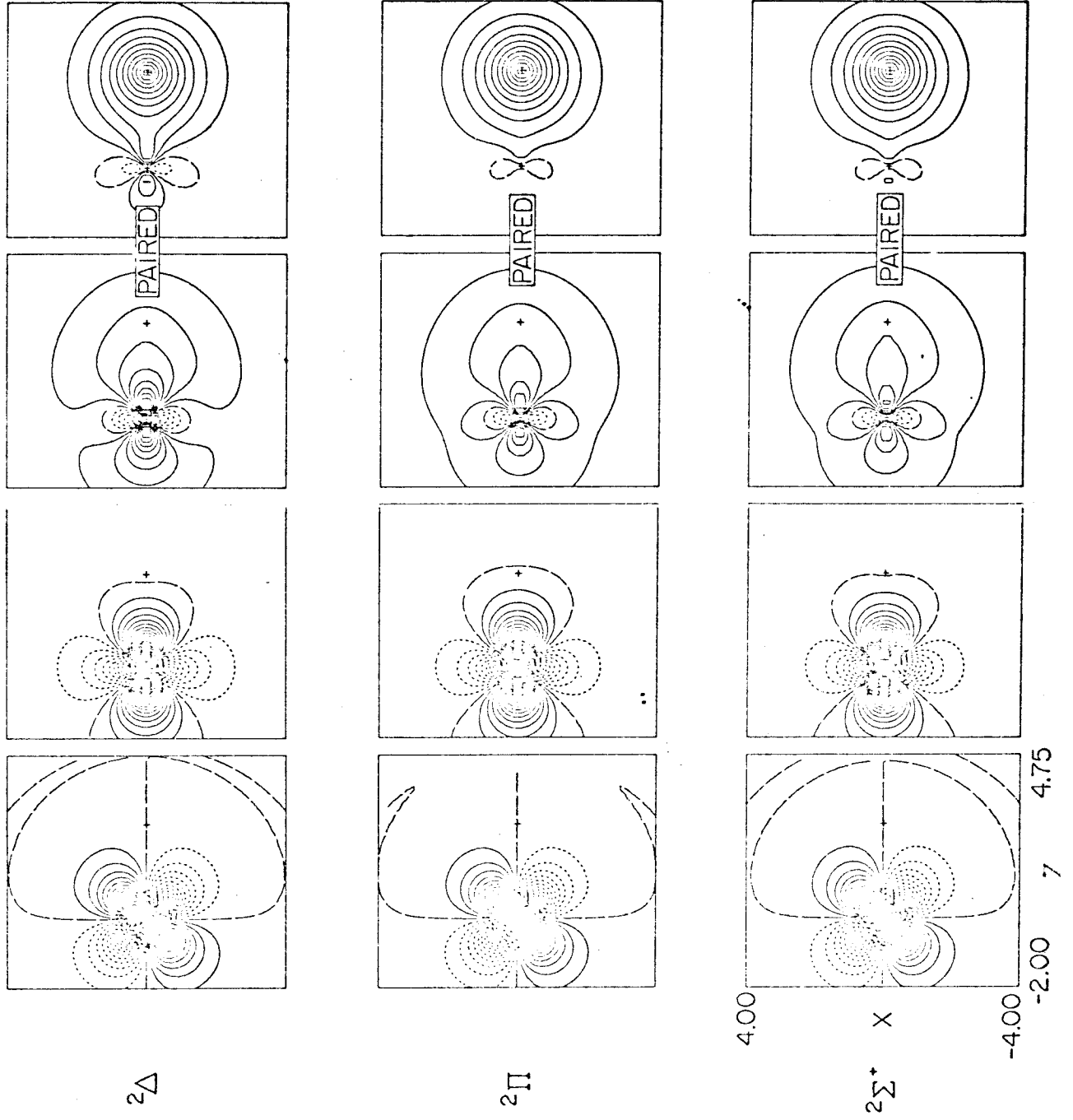


11. Potential curves of NiH from GVB(1) calculations using the MEP.

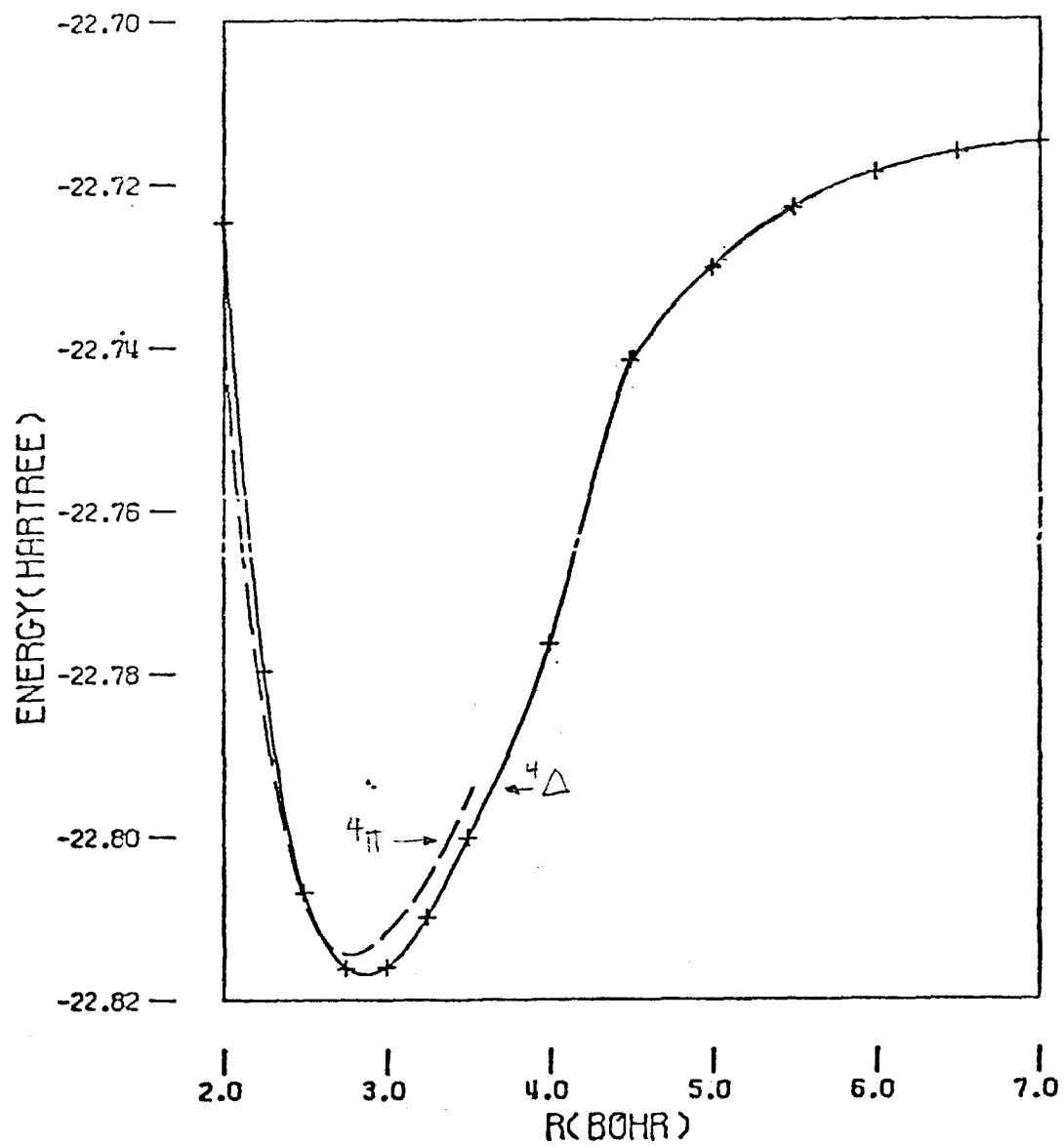
The arrow on the right indicates the energy for  $R = \infty$ .



12. GVB orbitals of NiH at R = 2.75 b.



13. Potential curves of FeH from GVB-CI calculations using the MEP.<sup>10</sup>





14. GVB orbitals of FeH at  $R = 2.75$ .

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