

## Fe AND Ni AB INITIO EFFECTIVE POTENTIALS FOR USE IN MOLECULAR CALCULATIONS

C.F. MELIUS\*

*Sandia Laboratories, Albuquerque, New Mexico 87115, USA*

and

B.D. OLAFSON† and W.A. GODDARD III

*Arthur Amos Noyes Laboratory of Chemical Physics‡, California Institute of Technology,  
Pasadena, California 91109, USA*

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We present effective potentials to replace the Ar core electrons of Fe and Ni. These effective potentials are obtained from ab initio ground state wavefunctions of Fe and Ni and are tested by comparing with ab initio SCF calculations for excited states of Fe, Fe<sup>+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ni, Ni<sup>+</sup>, Ni<sup>2+</sup>, and the FeH<sup>+</sup> molecule.

### 1. Introduction

It has long been clear that the chemistry of the heavier elements is determined by only the outer few (valence) electrons. However, in carrying out quantum mechanical calculations it has been necessary to include the core electrons along with the valence electrons, making the heavy atoms considerably more complicated and expensive than the light atoms. As a result there has been a great deal of interest in finding a way to eliminate the core electrons by replacing them with some type of effective potential [1–8].

In this paper we apply some of our recent techniques in obtaining highly accurate ab initio effective potentials in order to replace the core electrons of Fe and Ni atoms. The resulting effective potentials are tested on the ground and excited states of Fe, Fe<sup>+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Ni, Ni<sup>+</sup>, Ni<sup>2+</sup> and the FeH<sup>+</sup> molecule.

### 2. Effective potentials

Phillips and Kleinman [1] showed that by adding

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an additional pseudopotential to the valence HF hamiltonian one can redefine the Hartree–Fock one-electron hamiltonian so that the valence orbitals are smooth in the core region. However, it was found that the pseudo-orbitals and pseudopotentials were not unique [2]. Goddard and Kahn [5–7] found that by considering wavefunctions in which electron correlation effects are included in the core, they could obtain *unique* effective potentials directly from ab initio wavefunctions that would exactly reproduce the effect of the core for systems with one valence electron. They found that the resulting effective potentials depended upon the angular momentum of the valence electron (reflecting particularly the differing Pauli exclusion effects for different symmetries), leading to [6,7]

$$V^{\text{EP}}(r) = \sum_{l=0}^{\infty} V_l(r) |l\rangle\langle l|, \quad (1)$$

where  $V_l(r)$  is a radial function and

$$|l\rangle\langle l| \equiv \sum_{m=-l}^l |lm\rangle\langle lm|$$

is a projection operator onto states of angular momentum  $l$ . Kahn, Goddard, and Melius [6–8] applied

these ab initio effective potentials to the ground and excited states of a number of small molecules ( $\text{Li}_2$ ,  $\text{LiH}$ ,  $\text{Li}_2\text{H}$ ,  $\text{Be}$ ,  $\text{BH}$ ,  $\text{BH}_2$ ,  $\text{LiH}_2$ ) and their positive ions, finding that the energies and molecular properties are well described (energies generally to within 0.05 eV).

However, Melius, Surratt, Goddard and Kahn [7,9, 10, 11] showed that very similar effective potentials could also be obtained from HF wavefunctions. Melius and Goddard [10, 11] found that a particularly useful approach is to mix components of the core orbitals (of the same angular momentum) into the HF valence orbital such that the new orbital goes smoothly to zero at the origin. Since the resulting orbital is smoothly varying and has a small amplitude in the core region, it does not require core-like basis functions. The resulting orbital is called the coreless Hartree-Fock (CHF) orbital<sup>\*</sup>. This allows us to minimize the number of basis functions required to give an accurate description of the eigenstates of the potential, and greatly extends the size of systems we can consider.

In the earlier work [6-8]  $V_l(r)$  was obtained as a numerical function of  $r$ . However Melius, Kahn and Goddard [7] found that the computational costs could be reduced several orders of magnitude by expanding each radial function  $V_l(r)$  in terms of gaussian functions

$$V_l(r) = \sum_k c_k r^{n_k} \exp(-\zeta_k r^2). \quad (2)$$

In this case the general three-center integrals (for gaussian basis functions) were reduced to simple analytic functions in terms of the error function ( $\int^x e^{-\sigma^2} d\sigma$ ), Dawson's integral ( $e^{-x^2} \int_0^x e^{\sigma^2} d\sigma$ ), and  $e^{-x^2} \int_0^x e^{\sigma^2} (\text{erf } \sigma) d\sigma$ . As a result, the computation time for three-center effective potentials is reduced to that of simple nuclear attraction integrals.

We define the effective potential  $V^{\text{EP}}(r)$  by requiring that<sup>#</sup>

$$(h + V^{\text{EP}} + \hat{V}_{\text{val}}) \phi_{\text{val}} = \epsilon_v \phi_{\text{val}} \quad (3)$$

yields an eigenvalue  $\epsilon_v$  and eigenfunction  $\phi_{\text{val}}$  corresponding as close as possible to the orbital energy and

<sup>\*</sup> The CHF effective potential has been used in the calculation of alkali-alkali ion dimers. See refs. [10,12].

<sup>#</sup> Note that for atoms with one valence electron  $\hat{V}_{\text{val}} = 0$  and this term in (3) and (4) is omitted.

CHF orbital resulting from the ab initio calculations. (Here  $\hat{V}_{\text{val}}$  contains the potential terms due to the other valence orbitals.) We fit the parameters in (2) by projecting (3) onto appropriate basis functions  $\chi_\mu$  and requiring that

$$\langle \chi_\mu | (h + V^{\text{EP}} + \hat{V}_{\text{val}} - \epsilon_v) | \phi_{\text{val}} \rangle = 0 \quad (4)$$

is satisfied in a least squares sense.

### 3. Results and discussion

#### 3.1. Fe atom effective potential

The  $V_s$  and  $V_d$  effective potentials for Fe were defined using (4) so as to reproduce the  $\epsilon_{3d}$  and  $\epsilon_{4s}$  orbital energies and the  $\phi_{3d}$  and  $\phi_{4s}^{\text{CHF}}$  orbitals for the Hartree-Fock ground state  $^5D(4s^2 3d^6)$  of Fe.  $V_p$  was defined so as to reproduce  $\epsilon_{4p}$  and  $\phi_{4p}^{\text{CHF}}$  for the  $(4s)(4p)(3d)^6$  high spin state of Fe. The parameters defining  $V^{\text{EP}}$  for Fe [eq. (2)] are listed in table 1<sup>\*</sup>.

The Fe effective potential was tested on various states of Fe,  $\text{Fe}^+$ ,  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  <sup>##</sup>. In tables 2 and 3 we compare the total energies and orbital energies obtained using the Fe effective potential with the ab initio full-electron results. A basic assumption in the effective potential approach is that the core electrons in the molecule remain unchanged as the molecule is excited, ionized, or dissociated. In the exact wavefunction, the core electrons readjust in response to changes in the electronic configuration of the valence electrons. We therefore recalculated the ab initio

<sup>\*</sup> For angular momenta higher than the angular momenta of the core electrons, the  $V_l(r)$  of (1) are very similar (see refs. [6,7]). In this case (1) can be reduced to the form

$$V^{\text{EP}}(r) \approx V_d(r) + V_{s-d} |s\rangle\langle s| + V_{p-d} |p\rangle\langle p|,$$

where

$$V_{s-d} \equiv V_s - V_d; \quad V_{p-d} \equiv V_p - V_d$$

(all  $V_i$  are functions of the radial coordinate only).

<sup>##</sup> The Fe  $V_d$  potential is defined for the 3d orbital and may not be adequate for describing the Rydberg 4d orbital of Fe since the 4d orbital has a different shape in the core region of the 3s and 3p orbitals. (See refs. [10,11] for a discussion.) On the other hand, the 5s and 4s have similar shapes in the core region, so  $V_s$  should do well for Rydberg s orbitals. Likewise,  $V_p$  should do well for Rydberg p orbitals.

Table 1

The parameters for the Fe and Ni effective potentials. See eq. (2) for definitions of  $n$ ,  $\xi$ , and  $C$ . See footnote \* for the form of the total potential. All quantities in atomic units

$n$	Fe		Ni		
	$\xi$	$C$	$\xi$	$C$	
$V_d$	-1	0.0	-8.0	0.0	-10.0
	-1	19.88	-9.925	21.66	-9.827
	-1	0.591	-1.380	0.659	-1.247
	0	4.52	-12.66	5.02	-12.84
$V_{s-d}$	-2	0.980	7.968	0.959	7.465
	0	0.499	1.290	0.504	0.8480
	0	9.44	-51.14	8.87	-28.67
$V_{p-d}$	-2	0.388	4.457	0.465	4.807
	0	5.97	31.08	5.62	23.61

wavefunctions with the core orbitals frozen to be those of the Fe  $5D(4s^2 3d^6)$  ground state. The errors resulting from this frozen core assumption in Fe are shown in tables 2 and 3.

We see that the frozen core assumption is an important source of error in the effective potential approximation. This error is particularly serious for the transition elements since the 3d orbitals are close enough to the 3s and 3p orbitals of the core that significant core relaxation effects occur as the occupation number of the 3d orbitals changes, for example, from  $s^2 d^6$  to  $sd^7$  to  $d^8$ . The worst case is for  $d^8$  where the error in excitation energy is 0.5 eV out of 12 eV (i.e., 4%). On the other hand, changes in the 4s orbital occupation number do not seriously affect the core (e.g., for  $Fe^+ sd^6$  and  $Fe^{2+} d^6$  the error is less than 0.01 eV).

The results of tables 2 and 3 show that the excitation energies and orbital energies from the Fe effective potential are in reasonable agreement with the SCF results. The errors are generally of about the same magnitude as found in the frozen core approximation. Note that changes in the orbital coupling between the 4s and 3d shells (e.g., Fe  $s^2 d^6$  to  $Fe^+ sd^6$ ) lead to larger errors than do changes in the orbital coupling within the 3d shell (e.g., various states of Ni)<sup>††</sup>.

<sup>††</sup> The error results from the use of the pseudo-orbital (e.g.,  $\phi_{4s}^{CHF}$ ) in the 4s-3d exchange integral.

### 3.2. $Fe^{7+}$ effective potential

An alternative approach to obtain effective potentials is to bypass the  $V_{val}$  term in (3) and (4). Thus one can start with a fixed Fe core (say from the  $s^2 d^6$  state), solve for the 4s, 4p, 3d, etc. states of  $Fe^{7+}$ , and solve (4) for the  $V^{EP}$ . This type of approach was applied to Be-Ne and worked reasonably well [7, 13, 14].

However, the  $Fe^{7+}$  4s, 4p, and 3d orbitals are much tighter in size than the corresponding orbitals of the neutral system. Consequently, the use of the  $Fe^{7+}$  orbitals in (4) emphasizes a region of Hilbert space quite different from that appropriate for the neutral atoms. More importantly, the  $Fe^{7+}$  effective potential ignores the valence-valence interaction. Olafson, Goddard, Redondo-Muñoz and Wadt [15] have found that the replacement of the HF valence orbitals with pseudo-orbitals (such as the CHF orbital) leads to significant changes in the values of the valence-valence Coulomb and exchange integrals. They found that by including  $V_{val}$  in (3) these changes in the 4s-3d interactions are accounted for in the process of determining  $V^{EP}$ , leading to much more accurate results.

As expected, the  $Fe^{7+}$  effective potential does quite poorly for the neutral states, as indicated in table 2 where the errors in excitation and ionization energies are of the order of 1 to 2 eV for all states. Using the  $Fe^{7+}$  potential, the orbital energies for the  $(4s)^2 (3d)^6$  state are -0.2163, -0.7460, and -0.5925 compared with -0.2537, -0.6872, and -0.5358 for the SCF results. These errors of  $\approx 1$  eV are over 10 times the error obtained from the effective potential using the Fe neutral orbitals.

### 3.3. Ni atom effective potential

A similar approach was used for the Ni atom. The Ni potential is listed in table 1. The total energies and orbital energies for various tests on Ni,  $Ni^+$ , and  $Ni^{2+}$  are compared in tables 2 and 3. The quality of the Ni effective potential is comparable to that of the Fe.

### 3.4. $FeH^+$ molecule

In order to provide a more severe test for the usefulness of these effective potentials, we have solved

Table 2  
Energies for various states of Fe and Ni atoms (energies in hartrees)

Electronic state a)	Excitation energy	Error in excitation energy b)			
		ab initio SCF	ab initio frozen core	effective potential	
			based on neutral atom	based on Fe <sup>7+</sup>	
Fe	s <sup>2</sup> d <sup>6</sup>	0 c)	0 c)	0 d)	0 d)
	s <sup>1</sup> d <sup>7</sup>	0.1491	+0.0057	-0.0060	-0.0429
	s <sup>0</sup> d <sup>8</sup>	0.4245	+0.0201	-0.0051	-0.0381
Fe <sup>+</sup>	s <sup>1</sup> d <sup>6</sup> e)	0.2441	+0.0000	-0.0006	-
	s <sup>1</sup> d <sup>6</sup>	0.2284	+0.0000	-0.0138	-0.0376
	s <sup>2</sup> d <sup>5</sup>	0.3132	+0.0094	+0.0013	+0.0535
	s <sup>0</sup> d <sup>7</sup>	0.3299	+0.0062	+0.0007	-0.0781
Fe <sup>2+</sup>	s <sup>0</sup> d <sup>6</sup>	0.7801	+0.0002	+0.0087	-
	s <sup>1</sup> d <sup>5</sup>	0.8792	+0.0113	-0.0122	-0.0385
Fe <sup>3+</sup>	s <sup>0</sup> d <sup>5</sup>	1.8229	+0.0139	+0.0311	-
Ni	s <sup>2</sup> d <sup>8</sup>	0 f)	0 f)	0 g)	0 g)
	s <sup>2</sup> d <sup>8</sup> h)	0.0927	+0.0000	+0.0002	-
	s <sup>1</sup> d <sup>9</sup>	0.0894	+0.0059	-0.0042	-
	s <sup>0</sup> d <sup>10</sup>	0.3623	+0.0198	-0.0096	-
Ni <sup>+</sup>	s <sup>1</sup> d <sup>8</sup>	0.2526	+0.0000	-0.0069	-
	s <sup>2</sup> d <sup>7</sup>	0.4472	+0.0090	+0.0027	-
	s <sup>0</sup> d <sup>9</sup>	0.3059	+0.0061	-0.0015	-
Ni <sup>2+</sup>	s <sup>0</sup> d <sup>8</sup>	0.8313	+0.0002	+0.0094	-
	s <sup>0</sup> d <sup>8</sup> h)	0.9252	+0.0002	+0.0095	-
	s <sup>1</sup> d <sup>7</sup>	1.0609	+0.0103	-0.0018	-

a) Except where indicated, we have solved for the high spin state corresponding to the  $s^n d^m$  configuration. Since our emphasis is upon molecular studies we used the real forms of the orbitals in single spatial-configuration wavefunctions. Thus, the states are not necessarily eigenstates of  $\hat{L}^2$ . In addition, doubly-occupied 3d orbitals have slightly different shapes and orbital energies from singly-occupied 3d orbitals.

b) Error in excitation energy (energy difference from ground state) as compared with the ab initio SCF excitation energy.

c) Energy relative to -1261.3517h.

d) The total energies calculated for the  $s^2 d^6$  state of Fe using Fe and Fe<sup>7+</sup> effective potentials are -21.5583h and -21.2639h, respectively.

e) Orbital-coupling of 4s and 3d orbitals is the same as for Fe <sup>5</sup>D( $s^2 d^6$ ).

f) Energy relative to -1506.7345h.

g) The total energy calculated for the  $s^2 d^8$  high-spin state of Ni using the Ni effective potential is -39.1092h.

h) Spin state is a singlet.

for the lowest <sup>5</sup>Δ and <sup>5</sup>Σ<sup>+</sup> states of FeH<sup>+</sup> at  $R = 3a_0$  (close to the expected bond length) and at  $R = 100a_0$ . These calculations were carried out both for the HF wavefunction and for the GVB correlated wavefunction. The results are listed in table 4 where we compare the full-electron ab initio calculations to the eight-electron effective potential studies. For the <sup>5</sup>Δ state the error in the calculated bond energy is 0.0015h = 0.04 eV or 3% of the total bond energy of 0.047h = 1.27 eV<sup>◊</sup>. For the <sup>5</sup>Σ<sup>+</sup> state, the bond energy error is 0.0050h = 0.14 eV or 12 % of the calculated energy of 0.042h = 1.13 eV<sup>◊</sup>. The orbital ener-

gies are generally good to about 1 %. In addition the correlation energies and the natural orbital parameters of the correlated wavefunctions are within 1 % of the ab initio results. These cases represent a reasonably

◊ The FeH<sup>+</sup> calculation at  $R = 100a_0$  used the same orbital coupling as at  $R = 3a_0$  (i.e., the Fe 4s orbital and the H 1s orbitals are still singlet paired). This result in an  $E(R = 3a_0) - E(R = 100a_0)$  which is 0.0157h too large. Since both the ab initio and effective potential calculations use the same orbital coupling, this does not affect the analysis of the errors.

Table 3  
Comparison of orbital energies for ab initio (AI), frozen core (FC), and effective potential (EP) calculations for various states of Fe and Ni (energy in hartrees)

State a)	Orbital			State a)	Orbital		
	4s	3d singly occ.	3d doubly occ.		4s	3d singly occ.	3d doubly occ.
Fe $s^2d^6$	AI	-0.2537	-0.6872	Ni $s^2d^8$	AI	-0.2706	-0.7518
	FC	-0.2537	-0.6872		FC	-0.2706	-0.7518
	EP	-0.2538	-0.6842		EP	-0.2707	-0.7509
Fe $s^1d^7$	AI	-0.2103	-0.4325	Ni $s^2d^8c)$	AI	-0.2710	-0.6576
	FC	-0.2106	-0.4192		FC	-0.2710	-0.6584
	EP	-0.2170	-0.4249		EP	-0.2712	-0.6572
Fe <sup>+</sup> $s^1d^6b)$	AI	-0.5373	-1.0063	Ni $s^1d^9$	AI	-0.2170	-0.4733
	FC	-0.5374	-1.0065		FC	-0.2172	-0.4598
	EP	-0.5468	-1.0046		EP	-0.2198	-0.4720
Fe <sup>+</sup> $s^1d^6$	AI	-0.5536	-0.9952	Ni <sup>+</sup> $s^1d^8$	AI	-0.5804	-1.0802
	FC	-0.5538	-0.9954		FC	-0.5805	-1.0803
	EP	-0.5767	-0.9953		EP	-0.5969	-1.0842
Fe <sup>+</sup> $s^2d^5$	AI	-0.5925	-	Ni <sup>+</sup> $s^2d^7$	AI	-0.6324	-1.3818
	FC	-0.5941	-		FC	-0.6336	-1.4055
	EP	-0.5999	-		EP	-0.6401	-1.3956
Fe <sup>2+</sup> $s^0d^6$	AI	-	-1.3669	Ni <sup>2+</sup> $s^0d^8$	AI	-	-1.4747
	FC	-	-1.3678		FC	-	-1.4754
	EP	-	-1.3793		EP	-	-1.4899
Fe <sup>2+</sup> $s^1d^5$	AI	-0.9462	-	Ni <sup>2+</sup> $s^0d^8c)$	AI	-	-1.3803
	FC	-0.9487	-		FC	-	-1.3818
	EP	-0.9903	-		EP	-	-1.3961
Fe <sup>3+</sup> $s^0d^5$	AI	-	-2.0745	Ni <sup>2+</sup> $s^1d^7$	AI	-0.9992	-1.7885
	FC	-	-2.1112		FC	-1.0011	-1.8150
	EP	-	-2.1193		EP	-1.0347	-1.8143

a) See footnote a, table 2.

b) See footnote e, table 2.

c) See footnote h, table 2.

strong test since the effective potential was obtained from the neutral Fe atom (26 electrons) whereas the electron population on the Fe is  $\approx 24.7$  ( $^5\Delta$ ) and  $\approx 24.9$  ( $^5\Sigma^+$ ) electrons.

### 3.5. Reduction in computational effort

The gaussian basis set for the ab initio wavefunctions of Fe or Ni requires 14 s, nine sets of p, and five sets of d gaussian functions [16]. Using the CHF effective potential no p functions are necessary and only four of the 14 s functions are required. (The exponents of the four s functions were optimized so as to describe both Fe  $s^2d^6$  and Fe<sup>+</sup>  $sd^6$  states to within  $0.0002h = 0.005$  eV. Contracting the inner two s functions together leads to an error of  $0.0003h$  for Fe and  $0.0001h$  for Fe<sup>+</sup>.)

For the FeH<sup>+</sup> molecule, 44 contracted basis functions (81 primitives) were used in the ab initio calculation, requiring 1174 seconds on a CDC 6600 to evaluate the two-electron integrals and 9 seconds for the one-electron integrals (an additional 1 second was required to evaluate the effective potential integrals over this basis set). On the other hand, only 23 basis functions (44 primitives) are needed after removing the core basis functions, requiring 192 seconds for the two-electron integrals and 3 seconds for the one-electron integrals (including the effective potential). The ab initio SCF calculation (44 basis functions) required 80 seconds per iteration while the effective potential SCF calculation (23 basis functions) required 10 seconds per iteration with fewer iterations needed. Thus the savings are about one order of magnitude while retaining an accuracy consistent with ab initio

Table 4  
 $^5\Delta$  and  $^5\Sigma^+$  states of  $\text{FeH}^+$  ( $R = 3a_0$ ). All energies in hartrees

	$^5\Delta$ state			$^5\Sigma^+$ state		
	ab initio	effective potential		ab initio	effective potential	
		big basis	small basis		big basis	small basis
$E(3a_0) - E(100a_0)^a$	-0.0617	-0.0599	-0.0598	-0.0567	-0.0617	-0.0611
orbital energies						
$\epsilon_{d\sigma}$	-0.9464	-0.9379	-0.9362	-0.8422 b)	-0.8501 b)	-0.8474 b)
$\epsilon_{d\pi}$	-0.9853	-0.9864	-0.9847	-0.9934	-1.0009	-0.9978
$\epsilon_{d\delta}$	-0.9545	-0.9624	-0.9608	-1.0248	-1.0247	-1.0222
$\epsilon_{d\delta}$	-0.8386 b)	-0.8421 b)	-0.8400 b)	-1.0248	-1.0247	-1.0222
bond pair quantities <sup>c)</sup>						
$\epsilon_{1\text{NO}}$	-0.6849	-0.6901	-0.6899	-0.6729	-0.6785	-0.6774
$\epsilon_{2\text{NO}}$	-1.1515	-1.1588	-1.1514	-1.0619	-1.0852	-1.0843
$C_2$	-0.1435	-0.1415	-0.1444	-0.1664	-0.1590	-0.1594
$S_{ab}$	0.7468	0.7498	0.7453	0.7113	0.7225	0.7218
$\Delta E$	-0.0188	-0.0184	-0.0189	-0.0218	-0.0208	-0.0210

a) See ref. [15].

b) This orbital is doubly-occupied.

c) 1NO and 2NO indicate the natural orbitals of the correlated pair,  $C_1\phi_1^2\text{NO} + C_2\phi_2^2\text{NO}$ ;  $C_2$  is the CI coefficient ( $C_1^2 + C_2^2 = 1$ );  $\Delta E$  is the correlation energy of the pair;  $S_{ab}$  is the overlap of the GVB orbitals of the pair. See ref. [17].

wavefunctions. For calculations on bigger molecules for which more atoms are replaced by effective potentials, the savings in computational effort becomes increasingly more significant.

#### 4. Conclusions

We consider these results to be quite encouraging. The use of effective potentials reduces the complexity of treating transition metal atoms to that more comparable with studying a first row atom such as F while retaining near ab initio quality results. This should allow more extensive studies of extended transition metal systems.

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