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New Model Potential for Pseudopotential Calculations*

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The use of model potentials in pseudopotential calculations is discussed, and a set of desirable criteria for model potentials is suggested. The Hellmann potential and the Abarenkov and Heine potential are examined, and it is shown that both potentials are useful, but neither fully satisfies the suggested desiderata. A new potential of the form, $V(r) = -Z/r + \sum_l B_l P_l / r^2$, where P_l is the projection operator over the subspace of spherical harmonics of a given l , is proposed. A physical interpretation of the potential in terms of a "Pauli force" and a polarized core is given. Ionization energies for excited S , P , D , and F states for one-valence-electron atoms are calculated. The new potential is also applied to two-valence-electron atoms, and their calculated valence-state energies are shown to be in good agreement with experimental values.

I. INTRODUCTION

For most atomic and molecular systems it would be advantageous to treat the valence electrons without explicitly considering the core electrons. In particular, for a one-valence-electron system, it would be desirable to be able to work with an eigenvalue equation of the form

$$(-\frac{1}{2}\nabla^2 + V_M)\phi_v = E_v\phi_v, \quad (1)$$

where V_M is a modified potential including all valence-core interactions, E_v is the orbital energy of the valence electron, and ϕ_v is a valence pseudowavefunction which need not be orthogonal to the core orbitals. An equation of this form has in fact been derived using pseudopotential theory.^{1,2}

In the terminology of Szasz and McGinn,³ V_M is defined by

$$V_M = V_{\text{HF}} + V_P + V_R, \quad (2)$$

where V_{HF} is the standard Hartree-Fock potential, V_P is a polarization potential,⁴ and V_R is a pseudopotential. V_R is defined by the equation

$$V_R = \sum_i \langle \phi_i | \phi_v \rangle (E_v - E_i) \phi_i / \phi_v, \quad (3)$$

where the sum is taken over all core orbitals ϕ_i . E_i and E_v are the orbital energies of the core orbitals and the valence orbital, respectively, and ϕ_v is a pseudowavefunction obtained from the Hartree-Fock valence orbital by the transformation

$$\phi_v = \phi_{v,\text{HF}} + \sum_i \alpha_i \phi_i, \quad (4)$$

where $\alpha_i = \langle \phi_v | \phi_i \rangle$.

Properties of one-valence-electron systems have been successfully calculated using Eq. (1).⁵ There are, however, several disadvantages in using this particular modified potential. (1) One of the purposes of the pseudopotential method is to remove the core electrons from the calculation. However, to obtain the modified potential, the core orbitals must be known, and from a practical viewpoint, this limits the systems which can be considered. (2) Since the pseudopotential is a function of the pseudowavefunction, Eq. (1) must be solved

in an iterative manner. (3) The modified potential is mathematically complicated, hence difficult to use in studying large molecular systems.

The exact pseudopotential formalism is certainly useful as a calculational technique, nevertheless, it has been suggested by Weeks and Rice that "The advantage of a pseudopotential formalism lies not in the formal exact solution but in the physical insights it gives and the models it suggests."⁶ Sharing this viewpoint, in this paper we will examine what properties are desirable in a model potential, investigate two currently used models, and propose a new potential. Finally, the new potential will be used in calculations on one- and two-valence-electron systems.

II. MODEL POTENTIALS

In what we call a *model potential*, we alter Eq. (1) by substituting a model potential for the modified potential, replacing the pseudowavefunction by a model wavefunction, but (hopefully) leaving the eigenvalue unchanged. The most important conditions that an adequate model potential should satisfy are as follows:

- (i) The model potential form should be applicable to many different core systems.
- (ii) There should be a simple method of obtaining the necessary parameters.
- (iii) The potential should be variational, i.e., by varying the model wavefunction for the state used in the parameterization the calculated energy should converge from above to the experimental value.
- (iv) The potential should permit the accurate prediction of several experimental quantities not used in its parameterization.
- (v) The potential should be a function of the l value of the valence electron. This property will be referred to as l flexibility.
- (vi) The potential should be Coulombic for large r , by which we mean that the dominant term in the potential for large r should go as $1/r$.
- (vii) The model potential should have a physical basis.

Conditions (i)–(iv) are obviously necessary for a model

potential to be useful. Conditions (v) and (vi) are required by the pseudopotential formalism; the modified potential has these properties, and calculations with model potentials that do not have them have failed.⁷ Condition (vii) simply states that the model must embody some of the essential physics of the system.

Two model potentials have been used extensively. They are the Hellmann potential,⁸

$$V = -Z/r + A \exp(-2\kappa r)/r, \quad (5)$$

and the Abarenkov and Heine potential,⁹

$$V = \sum_{l=0}^{\infty} B_l P_l, \quad r < R_c, \\ = -Z/r, \quad r > R_c. \quad (6)$$

In both Eqs. (5) and (6) Z is the net charge of the core system. In Eq. (5) A and κ are adjustable parameters, chosen to fit certain valence-state ionization energies and allowing for partial variationality.³ In Eq. (6) B_l is an adjustable constant for a given l valence state, R_c is a "core radius," and P_l is the projection operator over the subspace of spherical harmonics of a given l .

Although simple in principle, parameterization of the Hellmann potential presents algebraic difficulties.¹⁰ There are many systems, such as Li and Be^+ , for which the method fails and no parameters can be obtained. The potential does not have l flexibility and it is not variational, but it is Coulombic for large r . The Hellmann potential is repulsive for small r , which can be understood in terms of a "Pauli force" which prevents the valence electrons from collapsing into the core.

The parameters for the Abarenkov and Heine potential can be chosen such that the potential is variational; however, this requires the use of an extensive one-

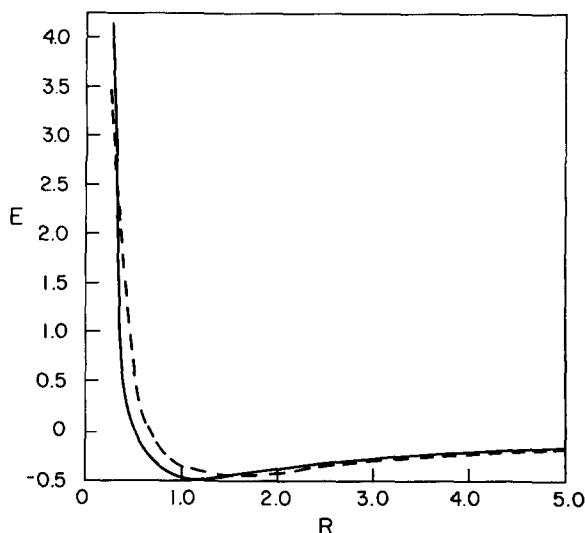


FIG. 1. A comparison of the Hellmann potential (---) and the AFP (—) for S states of Na. The Hellmann potential parameters are from Ref. 10. E and R are in atomic units.

electron model wavefunction.⁶ The potential is Coulombic for large r and has l flexibility. The potential does have a physical basis, as it can be justified via "core-valence nonpenetrability" arguments.⁶ However, the core radius value is somewhat arbitrary, and the discontinuity in the potential at this point is unphysical.

In summary, both the Hellmann and Abarenkov and Heine potentials are useful, but neither fully satisfies the desiderata (i)–(vii) for a one-electron model potential.

III. ATOMIC FUES POTENTIAL

We propose the model potential form

$$V(r) = -\frac{Z}{r} + \sum_{l=0}^{\infty} \frac{B_l P_l}{r^2}. \quad (7)$$

Here B_l , P_l , and Z have the same meanings as in Eq. (6). This potential resembles the Fues potential employed in studying the vibrations of diatomic molecules^{11,12}; thus Eq. (7) will be referred to as the atomic Fues potential (AFP), and written $V_{\text{AFP}}(r)$. Like the Hellmann potential, the AFP is repulsive for small r , due to the "Pauli force." Like the Abarenkov and Heine potential, the AFP has l flexibility.

The AFP, however, has one significant property that both the above potentials lack—it has simple eigenvalues and eigenfunctions. The eigenvalue equation,

$$\left[-\frac{1}{2}\nabla^2 + V_{\text{AFP}}(r)\right]\phi_v = E_v \phi_v, \quad (8)$$

has the solutions¹¹

$$E_v = -2Z^2/\{2P+1 + [(2l+1)^2 + 8B_l]^{1/2}\}^2, \\ P=0, 1, 2, \dots, \quad (9)$$

TABLE I. Parameters B_l for the atomic Fues potential.^{a,b}

Atom	Z	B_S	B_P	B_D	B_F
Li	1	0.46768	-0.05970	-0.00232	0.00448
Na	1	0.51047	0.18288	-0.02450	-0.00000
K	1	0.68234	0.37829	-0.35380	-0.02233
Rb	1	0.72657	0.47095	-0.55508	-0.04008
Cs	1	0.81277	0.57809	-1.02026	-0.07531
Be^+	2	0.63018	-0.06735	-0.00333	0.00112
Mg^+	2	0.85894	0.43336	-0.07455	-0.00671
Ca^+	2	1.22213	0.86815	-1.48144	-0.06269
Sr^+	2	1.35694	1.08377	-1.25970	-0.13286
Ba^+	2	1.55449	1.32740	-1.29532	-1.04950
Ra^+	2	1.52345	1.40605	-1.07693	-1.12080
Zn^+	2	0.64480	0.21803	0.06495	-0.04727
Cd^+	2	0.71265	0.31424	0.17566	-0.12693
Hg^+	2	0.59937	0.23166	0.22630	-0.13931

^a The parameters are defined by Eq. (9) and are in atomic units.

^b Experimental energies used in Eq. (9) and quoted in following tables are from C. Moore, Natl. Bur. Std. (U.S.) Circ. No. 467 (1949, 1952, 1958).

TABLE II. Predicted *S* valence-state ionization energies.^{a,b}

Atom	<i>n</i>	$-E_{n+1S}$		$-E_{n+2S}$		$-E_{n+3S}$		$-E_{n+4S}$	
		Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl
Li	2	0.07461	0.07416	0.03882	0.03846	0.02375	0.02363	0.01601	0.01594
Na	3	0.07243	0.07156	0.03800	0.03744	0.02335	0.02313	0.01579	0.01566
K	4	0.06513	0.06369	0.03517	0.03443	0.02197	0.02157	0.01501	0.01478
Rb	5	0.06355	0.06176	0.03453	0.03361	0.02166	0.02115	0.01486	0.01454
Cs	6	0.06072	0.05863	0.03339	0.03229	0.02109	0.02048	0.01451	0.01415
Be ⁺	2	0.26856	0.26719	0.14383	0.14310	0.08943	0.08903	0.06094	0.06069
Mg ⁺	3	0.23735	0.23441	0.13130	0.12973	0.08320	0.08231	0.05740	0.05686
Ca ⁺	4	0.20266	0.19851	0.11661	0.11420	0.07566	0.07424	0.05303	0.05213
Sr ⁺	5	0.19270	0.18779	0.11222	0.10932	0.07335	0.07164	0.05167	0.05059
Ba ⁺	6	0.18006	0.17460	0.10654	0.10322	0.07033	0.06834	0.04987	0.04861
Ra ⁺	7	0.18192	0.17508	0.10738	0.10330	0.07078	0.06835	0.05014	0.04860
Zn ⁺	4	0.26624	0.25715	0.14292	0.13844	0.08899	0.08660	0.06069	0.05928
Cd ⁺	5	0.25614	0.24317	0.13892	0.13243	0.08701	0.08351	0.05957	0.05750
Hg ⁺	6	0.27361	0.25311	0.14581	0.13603	0.09040	0.08528	0.06148	0.05851

^a All energies in atomic units.^b Calculated energies obtained using Eq. (9).

and

$$\phi_v = r^{a_l+1} \exp[-(-2E_v r)^{1/2}] \times F[-2P, 2a_l+2, 2(-2E_v)^{1/2}r], \quad (10)$$

where

$$a_l = -\frac{1}{2} + \frac{1}{2}[(2l+1)^2 + 8B_l]^{1/2} \quad (11)$$

and *F* is the confluent hypergeometric function.

This property is valuable in the light of the desirable criteria for a model potential. Using the ground valence-state ionization energy for a given *l*, Eq. (9) determines the corresponding *B_l* trivially. The potential thus obtained is variational, since it is based on an eigenvalue equation. Parameters can be obtained for all one-

valence-electron systems for which the appropriate ionization energies are known.

In addition, excited valence-state energies can be obtained from Eq. (9) simply by substituting the appropriate higher values for *P*. This is in contrast with other model potentials where the determination of an excited valence-state energy requires a variational calculation in which the orthogonality of the model wavefunction to other valence-model wavefunctions must be preserved.

IV. ONE-VALENCE-ELECTRON SYSTEMS

In Table I parameters obtained using ground-state ionization energies are listed for a number of one-

TABLE III. Predicted *P* valence-state ionization energies.^a

Atom	<i>n</i>	$-E_{n+1P}$		$-E_{n+2P}$		$-E_{n+3P}$		$-E_{n+4P}$	
		Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl
Li	2	0.05708	0.05722	0.03189	0.03197	0.02033	0.02037	0.01408	0.01410
Na	3	0.05145	0.05092	0.02949	0.02919	0.01909	0.01892	0.01336	0.01325
K	4	0.04781	0.04691	0.02789	0.02736	0.01825	0.01794	0.01287	0.01267
Rb	5	0.04629	0.04526	0.02721	0.02659	0.01789	0.01752	0.01265	0.01242
Cs	6	0.04467	0.04350	0.02648	0.02576	0.01750	0.01707	0.01242	0.01214
Be ⁺	2	0.22913	0.22950	0.12780	0.12810	0.08148	0.08159	0.05641	0.05646
Mg ⁺	3	0.18756	0.18517	0.10993	0.10844	0.07214	0.07124	0.05095	?
Ca ⁺	4	0.16359	0.16022	0.09892	0.09677	0.06620	?	0.04739	?
Sr ⁺	5	0.15417	0.15054	0.09444	0.09226	0.06373	0.06219	0.04589	?
Ba ⁺	6	0.14494	0.14114	0.08998	0.08746	0.06124	?	0.04436	?
Ra ⁺	7	0.14223	0.13821	0.08865	0.08396	0.06049	?	0.04390	?
Zn ⁺	4	0.20299	0.19770	0.11675	0.11373	0.07573	0.07498	0.05307	0.05050
Cd ⁺	5	0.19572	0.18825	0.11359	0.10909	0.07406	0.07156	0.05209	0.05072
Hg ⁺	6	0.20192	0.18742	0.11628	0.10892	0.07549	0.07120	0.05293	0.05075

^a See Footnotes a and b, Table II.

TABLE IV. Predicted D valence-state ionization energies.^a

Atom	n	$-E_{n+1}D$		$-E_{n+2}D$		$-E_{n+3}D$		$-E_{n+4}D$	
		Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl
Li	3	0.03127	0.03127	0.02001	0.02001	0.01389	0.01389	0.01021	0.01021
Na	3	0.03140	0.03143	0.02008	0.02010	0.01393	0.01395	0.01023	0.01024
K	3	0.03366	0.03467	0.02122	0.02198	0.01459	0.01510	0.01064	0.01098
Rb	4	0.03523	0.03639	0.02200	0.02279	0.01503	0.01553	0.01092	0.01125
Cs	5	0.03964	0.04011	0.02413	0.02436	0.01622	0.01635	0.01165	0.01173
Be ⁺	3	0.12508	0.12508	0.08004	0.08003	0.05558	0.05560	0.04083	0.04082
Mg ⁺	3	0.12690	0.12734	0.08097	0.08130	0.05612	0.05633	0.04117	0.04131
Ca ⁺	3	0.18221	0.17719	0.10751	0.10486	0.07085	0.06934	0.05018	0.04925
Sr ⁺	4	0.16985	0.16232	0.10184	0.09757	0.06779	0.06528	0.04835	0.04677
Ba ⁺	5	0.17170	0.15776	0.10270	0.09492	0.06826	0.06371	0.04863	0.04578
Ra ⁺	6	0.16106	0.14963	0.09772	0.09105	0.06554	0.06155	0.04699	0.04445
Zn ⁺	4	0.12340	0.12258	0.07918	0.07859	0.05508	0.05469	0.04052	0.04025
Cd ⁺	5	0.12078	0.11918	0.07783	0.07667	0.05429	0.05352	0.04002	0.03949
Hg ⁺	6	0.11962	0.11765	0.07723	0.07584	0.05394	0.05292	0.03980	0.03915

^a See Footnotes a and b, Table II.

valence-electron systems. In Tables II–V predicted excited-state ionization energies for S , P , D , and F states, respectively, are given and compared to experimental values. In general, the AFP very successfully predicts the excited-state energies.

In Fig. 1 the Na S valence-state AFP is compared to the Hellmann potential.¹⁰ We see that the AFP is similar to the Hellmann potential with none of the concomitant mathematical disadvantages of parameterization, variationality, and l flexibility.

The physical nature of the AFP can be further examined by inspecting the pseudopotential formalism. For a valence orbital which has core orbitals of the

same l , the pseudopotential V_R in Eq. (2) is nonzero. The pseudopotential is repulsive and is the source of the “Pauli force” which makes B_l positive. However, when there are no inner core orbitals with the same l value (the Li $1s^22p$ configuration for example), $V_R=0$ and the polarization potential V_P becomes important. In this case we might expect B_l to be negative; with two exceptions, Table I shows this to be the case.

Moreover, values of the respective B_l can be estimated from core polarizabilities. For one-valence-electron states of high n and l relative to the core, where valence-orbital penetration of the core is small, Born and Heisenberg¹³ (and later Mayer and Mayer¹⁴) have

TABLE V. Predicted F valence-state ionization energies.^a

Atom	n	$-E_{n+1}F$		$-E_{n+2}F$		$-E_{n+3}F$		$-E_{n+4}F$	
		Calc	Exptl	Calc	Exptl	Calc	Exptl	Calc	Exptl
Li	4	0.01999	0.01996	0.01389	?	0.01020	?	0.00781	?
Na	4	0.02000	0.02001	0.01389	0.01389	0.01020	0.01021	0.00781	0.00781
K	4	0.02005	0.02006	0.01392	0.01392	0.01022	0.01023	0.00782	0.00783
Rb	4	0.02009	0.02010	0.01394	0.01395	0.01024	0.01025	0.00783	0.00784
Cs	4	0.02017	0.02020	0.01399	0.01402	0.01027	0.01029	0.00785	0.00787
Be ⁺	4	0.07999	0.07999	0.05555	0.05554	0.04081	0.04081	0.03125	?
Mg ⁺	4	0.08006	0.08006	0.05559	0.05559	0.04084	0.04084	0.03127	0.03127
Ca ⁺	4	0.08058	0.08072	0.05589	0.05598	0.04103	0.04109	0.03139	0.03143
Sr ⁺	4	0.08124	0.08153	0.05627	0.05653	0.04127	0.04146	0.03155	0.03169
Ba ⁺	4	0.09108	0.10557	0.06186	0.07307	0.04474	0.05216	0.03386	0.03886
Ra ⁺	5	0.09196	0.10102	0.06235	0.06940	0.04504	?	0.03405	?
Zn ⁺	4	0.08043	0.08056	0.05581	0.05589	0.04097	0.04099	0.03136	0.03138
Cd ⁺	4	0.08118	0.08144	0.05624	0.05646	0.04124	0.04149	0.03153	0.03107
Hg ⁺	5	0.08130	0.08186	0.05630	0.05684	0.04129	0.04168	0.03157	0.03184

^a See Footnotes a and b, Table II.

TABLE VI. Parameters B_l evaluated from core polarizabilities.

Atom	n	l	α^a	B_l^b (calc)	B_l^c (exptl)
Li	2	1	0.025	-0.04218	-0.05970
Li	3	1	0.025	-0.04686	-0.05970
Li	3	2	0.025	-0.00312	-0.00232
Li	4	2	0.025	-0.00351	-0.00232
Na	3	2	0.17	-0.02124	-0.02450
Na	4	2	0.17	-0.02390	-0.02450
K	4	3	0.84	-0.02362	-0.02233
K	5	3	0.84	-0.02645	-0.02233
Rb	4	3	1.5	-0.04218	-0.04008
Rb	5	3	1.5	-0.04724	-0.04008
Cs	4	3	2.35	-0.06608	-0.07531
Cs	5	3	2.35	-0.07401	-0.07531
Be ⁺	2	1	0.007	-0.04724	-0.06735
Be ⁺	3	1	0.007	-0.05249	-0.06735
Be ⁺	3	2	0.007	-0.00350	-0.00333
Be ⁺	4	2	0.007	-0.00394	-0.00333
Mg ⁺	3	2	0.10	-0.04999	-0.07455
Mg ⁺	4	2	0.10	-0.04999	-0.07455
Ca ⁺	4	3	0.54	-0.06072	-0.06269
Ca ⁺	5	3	0.54	-0.06804	-0.06269
Sr ⁺	4	3	1.0	-0.11248	-0.13286
Sr ⁺	5	3	1.0	-0.12597	-0.13286

^a Core polarizability from Ref. 14. The polarizabilities are in units of 10^{-24} cm³.

^b Values obtained using Eq. (14). The B_l are in atomic units.

^c Values from Table I.

given the relation

$$E_{\text{exp}}(n, l) - E_{\text{H}}(n, l) = -\frac{1}{2}\alpha e^2 \langle r^{-4} \rangle_{\text{H}}. \quad (12)$$

$E_{\text{H}}(n, l)$ is the energy of the hydrogenic wavefunction with appropriate n and l , $\langle r^{-4} \rangle_{\text{H}}$ is the expectation value of r^{-4} for this state, e is the electronic charge, and α is the core polarizability. If $E_{\text{exp}}(n, l)$ is determined by the AFP, we have

$$\begin{aligned} & \langle \phi_{\text{AFP}}(P, l) | -\frac{1}{2}\nabla^2 - (Z/r) + (B_l/r^2) | \phi_{\text{AFP}}(P, l) \rangle \\ & - \langle \phi_{\text{H}}(n, l) | -\frac{1}{2}\nabla^2 - (Z/r) | \phi_{\text{H}}(n, l) \rangle \\ & \cong \langle \phi_{\text{H}}(n, l) | B_l/r^2 | \phi_{\text{H}}(n, l) \rangle = -\frac{1}{2}\alpha e^2 \langle r^{-4} \rangle_{\text{H}}. \end{aligned} \quad (13)$$

First-order perturbation theory has been used to obtain Eq. (13). Rearranging (13), an equation for B_l is obtained,

$$B_l \cong -\frac{1}{2}\alpha e^2 \langle r^{-4} \rangle_{\text{H}} / \langle r^{-2} \rangle_{\text{H}}. \quad (14)$$

In Table VI the B values estimated from Eq. (14) are compared to those of Table I.¹⁵

We conclude that the B_l values can be understood in terms of a "Pauli force" and an effective dipole representing a polarized core system.

V. TWO-VALENCE-ELECTRON SYSTEMS

As in the one-valence-electron case, our viewpoint is that the pseudopotential formalism should be used in

developing a model potential approach. Szasz¹⁶ has shown that the two-valence-electron energy can be written in the form

$$E_v = E_{\text{total}} - E_{\text{core}} = \langle \psi(1, 2) | H_{12}^M | \psi(1, 2) \rangle, \quad (15)$$

where $\psi(1, 2)$ is a two-electron pseudowavefunction and

$$H_{12}^M = \sum_{i=1}^2 \left[-\frac{1}{2}\nabla^2 + V_M(i) + W_R(i) \right] + \frac{h_0}{r_{12}}. \quad (16)$$

Here the modified potential V_M is formally identical with the modified potential of the one-valence-electron system. The factor h_0 is close to one, and can be set equal to one with little loss of accuracy. The W_R terms do not appear in the one-electron problem. Like the pseudopotential, they are functions of both core and valence orbitals.¹⁶

The energy of Eq. (15) can be partitioned,

$$E_v = E_v^0 + E_v^1, \quad (17)$$

$$\begin{aligned} E_v^0 = \langle \psi(1, 2) | & -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + V_M(1) \\ & + V_M(2) + (h_0/r_{12}) | \psi(1, 2) \rangle, \end{aligned} \quad (18)$$

$$E_v^1 = \langle \psi(1, 2) | W_R(1) + W_R(2) | \psi(1, 2) \rangle. \quad (19)$$

We only consider here two-valence-electron cases in which the valence electrons occupy S orbitals. As in the one-electron case, we seek to replace the modified potential by the AFP. Accordingly, E_v^0 values using the AFP given in Table I and the wavefunctions

$$\psi(1, 2) = (ns)^2 = r_1^n r_2^n \exp[-\zeta(r_1 + r_2)], \quad (20)$$

where n is nonintegral, and n and ζ are determined variationally, were calculated. In Table VII these values are compared to the E_v^0 values obtained by Szasz¹⁶; the agreement shows that the modified potentials can be replaced by the model potentials without much effect.

The value of the E_v^1 term is typically -0.05 to -0.10 a.u. As the W_R operators make only small contributions to the energy, are complicated in form, and require the core orbitals, it is desirable to approximate them. From pseudopotential theory, it is known that the electron-electron repulsion between the valence electrons is overestimated when the appropriate integral is evaluated over pseudowavefunctions instead of wavefunctions.^{6,16} The W_R operators are correction terms which reduce the electron-electron repulsion to its proper value.

An alternate method of including these corrections is to evaluate the electron repulsion integral in Eq. (18) over a region which excludes "core space."⁶ This approach can be justified on the basis of "core-valence nonpenetrability" arguments. A similar approach is to scale down the value of h_0 below the values 0.94-1.00 used by Szasz. To proceed further here, we have arbitrarily set h_0 equal to 0.90, i.e., made the approx-

TABLE VII. Predicted energies and ionization potentials for two-valence-electron systems.^a

Atom	E^0 ^b (Model)	E^0 ^c (Modified)	E_{calc} ^d	I_{exptl}	I_{calc} ^e	I_{exptl}
Be	-0.9105	-0.9254	-0.9968	-1.0116	0.3278	0.3426
Mg	-0.7461	-0.7625	-0.8105	-0.8333	0.2581	0.2809
Ca	-0.5839	-0.5796	-0.6392	-0.6607	0.2031	0.2246
Sr	-0.5411	...	-0.5925	-0.6144	0.1873	0.2092
Ba	-0.4890	...	-0.5371	-0.5590	0.1696	0.1815
Ra	-0.4965	...	-0.5428	-0.5667	0.1699	0.1938
Zn	-0.8976	-0.8518	-0.9679	-1.0051	0.3079	0.3451
Cd	-0.8429	...	-0.9099	-0.9516	0.2887	0.3304
Hg	-0.9388	...	-1.0083	-1.0725	0.3192	0.3834

^a See Footnote a, Table II.^b Values obtained using Eqs. (18) and (20) with $h_0 = 1.0$.^c Values from Ref. 16.^d Values obtained using Eqs. (18) and (22) with $h_0 = 0.9$.^e Ionization energies calculated by the equation $I = E_{\text{calc}}(\text{two-valence-electron system}) - E_{\text{exptl}}(\text{one-valence-electron system})$.

imation

$$\langle \psi(1, 2) | W_R(1) + W_R(2) | \psi(1, 2) \rangle \\ \cong -0.1 \langle \psi(1, 2) | (\tau_{12})^{-1} | \psi(1, 2) \rangle. \quad (21)$$

Valence energies calculated using this approximation are compared to experimental values in Table VII. Wavefunctions were taken to have the form

$$\psi(1, 2) = C_1(ns)^2 + C_2(n'p)^2, \quad (22)$$

where n and n' are nonintegral. There are four non-linear variational parameters: n , n' , ζ , ζ' . Calculations using further configurations allowing for radial correlation made slight improvements in the energy.

The results indicate that the energetic effects of the W_R terms can be simply included in the calculation by reducing the value of h_0 .¹⁷

VI. CONCLUSIONS

The model-potential approach provides a simple method for making valence-electron calculations. Although guided by the pseudopotential formalism, the method does not require knowledge of the core orbitals or iterative solutions. The model potential suggested in this paper is certainly not optimal; however, it does have a number of desirable mathematical and physical properties. The AFP can be used to replace the modified potential in one or two-valence-electron systems. The small extra corrections in the two-electron case can either be ignored or approximated by scaling down the electron repulsion integral.

Although the model potential successfully reproduces the energy spectrum of the modified potential, this does not necessarily mean the model wavefunctions are close to the pseudowavefunctions. More work is needed in this regard, however, there are many interesting properties of atoms and molecules which are explicitly dependent only on the valence energy, such as ioniza-

tion energies, equilibrium geometries, force constants, and dissociation energies. It is for these properties that the model potential approach should be most useful. Applications of the AFP to molecules are being investigated.

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