Local approximations for the exchange interaction between valence and core electrons

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Local approximations to interelectronic exchange are tested by comparing frozen-core relativistic Hartree-Fock calculations with relativistic model-potential results. The calculations are identical except in the treatment of exchange. Two new local approximations are suggested which appear significantly better than the usual Slater-type potential at reproducing effects of exchange between core and valence electrons of atoms. Results are tabulated for average radii and one-electron energies in Ag and Rb. Errors arising from the local approximation of exchange have been reduced on the average by a factor of about 5 with no increase in the complexity of the calculations.

I. INTRODUCTION

Simplifications of the Hartree-Fock (HF) procedure are often useful in calculations of the interactions between valence electrons and closed-shell cores, especially in molecular and solid-state applications. Two essential components of most such simplications are (1) the mathematical separation of "valence" and "core" electrons and (2) a local approximation for exchange. The purpose of this paper is to test the accuracy of local approximations for the exchange between valence and core electrons and to suggest simple improvements to the common form of approximation based on the Slater term (see Sec. II).

The search for suitable simplications has led to various pseudopotential and model-potential (MP) approaches[1-4] as well as to frozen-core and polarizable frozen-core HF techniques.[5] The polarizable frozen-core method does not approximate exchange effects. When applied to relativistic HF wave functions, it appears to yield reliable results[6] but is much more tedious and time consuming than the corresponding MP calculation.

If the electron density of the core is known, the resulting Coulomb potential is easily found and, together with the polarization potential, may be incorporated into a model potential. The *only* difference remaining between the MP and polarizable frozen-core approaches then lies in the exchange term, which is nonlocal in the HF calculation but is usually approximated by a local potential in the MP treatment. Comparison of MP calculations with their corresponding frozen-core HF counterparts permits a direct evaluation of the local-exchange approximation used in the model potential.

In order to draw valid conclusions about a local exchange potential, it is obviously important that other aspects of the MP and HF calculations be identical. Otherwise, an inaccurate electron density, for example, might compensate for defic-

iencies in the representation of exchange. It is also important that the frozen-core HF calculation be accurate in order to guard against false conclusions based on incomplete calculations. In our results presented below, both relativistic and correlation effects are included, and the MP and corresponding HF calculations are identical except in the treatment of exchange.

II. SLATER-TYPE APPROXIMATIONS

Local exchange approximations are generally based on the Slater term[7] (atomic units are used throughout)

$$V_{xS} = -\tfrac{3}{2}\kappa\rho^{1/3} , \tag{1}$$

where $\kappa = (3/\pi)^{1/3}$ and ρ is the number density of electrons. Expression (1) is derived from the average exchange energy of a free-electron gas of constant density. With ρ taken to be the total density of atomic or ionic electrons, (1) has been used in Hartree-Fock-Slater[8] calculations to represent the sum of interelectronic and "self" exchange. Consideration of the energy-minimization procedure suggests that the value of the exchange potential (1) should be reduced by a factor of $\tfrac{2}{3}$,[9] as used in the Thomas-Fermi-Dirac calculations.[1] Frequently κ is taken to be an adjustable parameter.[10] The inclusion of self-exchange, which in principle should cancel the self-Coulombic repulsion, often creates difficulties in atomic calculations. In particular, the asymptotic form of the potential energy is wrong and requires an artificial "correction."[11]

In the MP applications discussed here, such difficulties are avoided since Eq. (1) is used only for interelectronic exchange and ρ is set equal to the core-electron density ρ_c. Thus the first type of MP calculation we consider uses[3]

$$V_{x0} = -\tfrac{3}{2}\lambda\kappa\rho_c^{1/3} , \tag{2}$$

to represent exchange between valence and core electrons. The parameter λ is adjusted to match experimental ionization energies. At large r, ρ_c drops rapidly to zero, and the total effective potential has the correct asymptotic behavior.

III. CALCULATIONS

We test V_{x0} [Eq. (2)] and two other simple local approximations for exchange by comparing relativistic MP and HF calculations which differ only in their treatment of the exchange interaction. Relativistic HF calculations (RHF-CP) are made with a version of the Desclaux[12] program modified to include core-polarization effects.[6,13]

$$V_{\text{pol}} = -\tfrac{1}{2}\alpha r^2 (r^2 + r_0^2)^{-3/2} , \qquad (3)$$

where the dipole polarizability α calculated by Fraga et al.[14] is adopted and the value of r_0 is adjusted to reproduce the experimental ground-state ionization energy. The MP calculations with core polarization (MP-CP) employ polarization potentials and densities identical to those found in the HF case. The λ parameter of V_{x0} [Eq. (2)] as well as a parameter in each of the other two approximations tested (see next section) is used to match energies of the lowest state of given symmetry to experiment, and hence to those obtained in RHF-CP calculations. The adjusted values of λ and other parameters are found in Table I.

In order to avoid complications arising from correlation effects among valence electrons, tests are performed on atoms with one valence electron. The atoms chosen, Rb and Ag, have enough electrons to be fairly typical of cases for which statistical approximations of exchange are usually thought to be appropriate. Furthermore, the presence of the $4d$ shell in Ag and its absence from Rb means that conclusions drawn from the tests with both atoms are not liable to be structure dependent.

In the tests, calculated ionization energies and average radii of the orbitals are compared. These quantities provide sensitive monitors of the overall potential. The energy tends to be more sensitive to the small-r region whereas the average radius is more influenced by the potential at large r. Comparisons are made for s, p, and d states of principal quantum number $n = 5$–9.

IV. TWO NEW LOCAL APPROXIMATIONS FOR EXCHANGE

The MP and HF energies and average radii of the $s_{1/2}$, $p_{1/2, 3/2}$, and $d_{3/2, 5/2}$ states are compared in Table II for Ag I and Rb I. The MP energies calculated using Eq. (2) are seen to be consistently

TABLE I. Parameters (in atomic units) used in the calculations.

Spectrum	α [a]	State	r_0 [b]	λ [c]	r_1 [d]	r_2 [e]
Rb	11.15	$s_{1/2}$	1.478	0.264	2.143	1.111
		$p_{1/2}$	1.581	0.297	2.253	1.115
		$p_{3/2}$	1.596	0.309	2.363	1.142
		$d_{3/2}$	1.767	0.293	2.748	1.293
		$d_{3/2}$	1.776	0.295	2.790	1.302
Ag	10.07	$s_{1/2}$	1.326	0.281	2.013	1.065
		$p_{1/2}$	1.279	0.230	1.895	1.018
		$p_{3/2}$	1.265	0.231	1.921	1.024
		$d_{3/2}$	1.377	0.365	2.607	1.157
		$d_{5/2}$	1.392	0.377	2.728	1.182

[a] Dipole polarizability of the parent-ion core from Fraga et al. (Ref. 14).

[b] Cutoff radius in polarization potential [Eq. (3)] adjusted to give experimental ionization energies (Ref. 17).

[c,d,e] Parameters λ, r_1, and r_2 as used in local potentials V_{x0}, V_{x1}, and V_{x2}, respectively (see text).

too high and the average radii too large for excited states.

To find better local representations of the exchange interaction, we return to the electron-gas model and note that the interaction of a single electron with an electron distribution of density ρ actually depends on the ratio p/p_F of the momentum p of the single electron to the Fermi momentum p_F of the distribution. The Slater potential (1) results only after averaging the factor[1,7]

$$\tfrac{4}{3}F(\eta) = \frac{2}{3}\left(1 + \frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right|\right), \quad \eta = p/p_F \quad (4)$$

over p in the range $0 < p < p_F$. For a valence electron interacting with a core, $p > p_F$. One may, therefore, expect Eq. (1) to overestimate the exchange. Indeed, this is confirmed by applications of Eq. (2), in which the adjusted values of λ are typically only 0.2 to 0.3 compared to the average electron-gas value of 1.0 used in the Slater potential (1). Furthermore, p/p_F should increase from about unity at $r = 0$ to much larger values at large r. Since $F(\eta) = \tfrac{1}{2}$ at $\eta = 1$ and decreases rapidly with increasing η the electron-gas model itself suggests that a Slater-type expression [Eq. (2)] will tend to overestimate exchange, especially at large r. We tried to improve on Eq. (2) by representing $F(\eta)$ as a decreasing function of r, $F(\eta) = \tfrac{1}{2}e^{-r/r_1}$,

$$V_{x1} = -\kappa \rho^{1/3} e^{-r/r_1}, \quad \kappa = (3/\pi)^{1/3} . \qquad (5)$$

TABLE II. Percent errors in ionization energies ϵ and in average valence-shell radii $\langle r \rangle$ of Rb and Ag as calculated by the model-potential method (MP) with three different local approximations to the exchange interaction between the valence electron and the parent-ion core as compared to frozen-core relativistic Hartree-Fock (RHF) results. All calculations include core polarization (CP) and are otherwise identical except for their treatment of exchange.

State	$\epsilon^{\text{RHF+CP}}$ (a.u.)	$100 \times (\epsilon^{\text{MP+CP}} - \epsilon^{\text{RHF+CP}})/\epsilon^{\text{RHF+CP}}$ (0)[a]	(1)[a]	(2)[a]	$\langle r \rangle^{\text{RHF+CP}}$ (a.u.)	$100 \times (\langle r \rangle^{\text{MP+CP}} - \langle r \rangle^{\text{RHF+CP}})/\langle r \rangle^{\text{RHF+CP}}$ (0)	(1)	(2)
Rb $ns_{1/2}$								
$n=5$	0.153514	0	0	0	5.182	1.81	0.00	0.27
6	0.061791	−1.10	0.01	−0.11	12.328	1.31	−0.06	0.06
7	0.033625	−0.90	0.03	−0.06	22.445	1.01	−0.04	0.04
8	0.021160	−0.75	0.03	−0.05	35.556	0.71	−0.06	−0.05
9	0.014543	−0.63	0.05	−0.03	51.666	0.63	0.02	−0.08
Rb $np_{1/2}$								
$n=5$	0.096197	0	0	0	7.178	0.35	−0.38	−0.24
6	0.045429	−0.53	0.07	−0.01	15.778	0.73	−0.15	−0.09
7	0.026665	−0.48	0.08	0.00	27.331	0.60	−0.18	−0.05
8	0.017560	−0.41	0.08	0.01	41.878	0.50	−0.13	−0.02
9	0.012442	0.09	0.09	0.02	59.424	0.37	−0.07	−0.10
Rb $np_{3/2}$								
$n=5$	0.095114	0	0	0	7.273	0.25	−0.43	−0.27
6	0.045076	−0.49	0.07	−0.01	15.908	0.64	−0.17	−0.03
7	0.026505	−0.45	0.09	0.00	27.504	0.48	−0.18	−0.01
8	0.017474	−0.38	0.08	0.02	42.091	0.48	−0.21	−0.05
9	0.012391	−0.33	0.08	0.02	59.676	0.29	−0.12	−0.15
Rb $nd_{3/2}$								
$n=5$	0.036405	0	0	0	17.003	1.97	0.55	0.85
6	0.022804	−0.64	−0.18	−0.26	29.437	1.57	0.42	0.72
7	0.015545	−1.04	−0.27	−0.42	44.889	1.33	0.43	0.61
8	0.011255	−0.77	−0.19	−0.31	63.346	1.00	0.37	0.34
9	0.008519	−0.70	−0.18	−0.27	84.815	1.09	0.38	0.51
Rb $nd_{5/2}$								
$n=5$	0.036392	0	0	0	17.019	1.94	0.53	0.85
6	0.022794	−0.64	−0.17	−0.27	29.461	1.54	0.45	0.67
7	0.015538	−0.77	−0.21	−0.32	44.918	1.28	0.25	0.50
8	0.011250	−0.76	−0.20	−0.29	63.379	1.10	0.30	0.50
9	0.008515	−0.69	−0.19	−0.29	84.848	1.05	0.06	0.22
Ag $ns_{1/2}$								
$n=5$	0.278419	0	0	0	3.174	4.25	0.38	0.69
6	0.084339	−0.31	0.32	0.30	9.130	0.32	−0.47	−0.44
7	0.041926	−0.33	0.28	0.26	18.052	0.34	−0.32	−0.30
8	0.025133	−0.27	0.24	0.21	29.967	0.28	−0.25	−0.30
9	0.016750	−0.22	0.20	0.19	44.879	0.27	−0.23	−0.24
Ag $np_{1/2}$								
$n=5$	0.143771	0	0	0	4.598	3.70	0.30	0.57
6	0.058252	−1.48	−0.05	−0.15	12.131	1.92	0.00	0.16
7	0.032111	−1.22	−0.02	−0.11	22.550	1.40	0.00	0.04
8	0.020383	−1.01	0.00	−0.07	35.951	1.06	0.00	0.11
9	0.014094	−0.84	0.01	−0.06	52.348	0.92	0.01	0.06
Ag $np_{3/2}$								
$n=5$	0.139576	0	0	0	4.744	3.50	0.30	0.55
6	0.057303	−1.47	−0.06	−0.17	12.341	1.97	0.06	0.16
7	0.031729	−1.22	−0.03	−0.12	22.829	1.42	0.03	0.10
8	0.020191	−1.02	−0.02	−0.09	36.300	1.06	−0.06	0.03
9	0.013983	−0.86	0.00	−0.06	52.766	0.84	0.05	0.11

TABLE II. *(Continued.)*

State	$\epsilon^{\text{RHF+CP}}$ (a.u.)	$100 \times (\epsilon^{\text{MP+CP}} - \epsilon^{\text{RHF+CP}})/\epsilon^{\text{RHF+CP}}$ (0)	(1)	(2)	$\langle r \rangle^{\text{RHF+CP}}$ (a.u.)	$100 \times (\langle r \rangle^{\text{MP+CP}} - \langle r \rangle^{\text{RHF+CP}})/\langle r \rangle^{\text{RHF+CP}}$ (0)	(1)	(2)
Ag $nd_{3/2}$								
$n=5$	0.056 319	0	0	0	10.380	0.02	−0.11	−0.06
6	0.031 450	−0.25	0.00	−0.04	20.920	0.43	−0.08	0.00
7	0.020 076	−0.28	0.00	−0.03	34.425	0.32	−0.05	−0.01
8	0.013 925	−0.26	0.01	−0.04	50.921	0.23	−0.10	−0.07
9	0.010 224	−0.22	0.03	0.00	70.419	0.20	0.20	0.14
Ag $nd_{5/2}$								
$n=5$	0.056 221	0	0	0	10.411	−0.03	−0.12	−0.08
6	0.031 400	−0.23	0.01	−0.03	20.964	0.42	−0.00	0.00
7	0.020 049	−0.26	0.01	−0.03	34.481	0.31	−0.03	0.05
8	0.013 909	−0.24	0.02	−0.02	50.988	0.15	0.02	0.06
9	0.010 213	−0.21	0.02	−0.01	70.435	0.24	−0.11	0.06

[a] Versions (0), (1), (2) used the local potentials V_{x0}, V_{x1}, and V_{x2}, Eqs. (2), (5), and (8) respectively, to represent the exchange interactions between the valence electron and the parent-ion core. In each case, the one free parameter was adjusted to match $\epsilon^{\text{MP+CP}}$ (and thus to the experimental ionization energy) for the lowest state of each symmetry.

Now r_1 can be adjusted to match the lowest energies of a given symmetry. With V_{x1} in place of V_{x0}, the MP results usually lie much closer to the HF values (see Table II).

Additional support for using V_{x1} in place of V_{x0} can be found in Fig. 1, where the ratio of the effective local exchange $V_{\text{xRHF}}(r)$ to $-\kappa\rho_c^{1/3}$ [Eq. (1)] is plotted. Here $V_{\text{xRHF}}(r)$ is calculated from the large and small components, P and Q respectively, of the radial Dirac equation, to be that local potential which when added to the other local potentials V_{es} (for the direct Coulomb interaction with a point nucleus and core electrons), V_{nucl} (for the effect of the finite size of the nucleus), and V_{pol} (for the core polarization) gives the same P and Q components as the RHF nonlocal exchange interaction. From the radial Dirac equation (see for example Desclaux[12]) it is easily found that

$$V_{\text{xRHF}} = c\left(\frac{d}{dr}Q - \frac{l^*}{r}Q\right)\Big/P$$
$$+\epsilon - V_{\text{es}} - V_{\text{nucl}} - V_{\text{pol}}, \qquad (6)$$

where $c \doteq 137$ is the velocity of light, $l^* = l$ for $j = l - \frac{1}{2}$, and $l^* = -l - 1$ for $j = l + \frac{1}{2}$, and ϵ is the one-electron orbital energy. Although V_{xRHF} has singularities wherever P vanishes, it still is apparent that $V_{\text{xRHF}}/(-\kappa\rho^{1/3})$ (the solid line in Fig. 1) is better represented by a decreasing function of r (as in V_{x1}) than by a constant (as in V_{x0}).

Another local approximation for exchange is also suggested, this one based on the fact that the exchange interaction arises from a reduction caused by the Pauli exclusion principle in the interelectronic Coulomb repulsion. The combined interelectronic Coulomb and exchange operator for a closed-shell core operating on a valence electron at r can be written

$$V_{\text{cx}} = \sum_c \left\langle \varphi_c(\vec{r}_c) \left| |\vec{r} - \vec{r}_c|^{-1}\left[2 - \exp\left(\frac{i}{\hbar}(\vec{p}_c - \vec{p})\cdot(\vec{r}_c - \vec{r})\right)\right] \right| \varphi_c(\vec{r}_c) \right\rangle, \qquad (7)$$

where $\varphi_c(\vec{r}_c)$ is a doubly occupied core orbital, $\vec{p}_c$ and $\vec{p}$ are momentum operators for core and valence electrons, respectively, and the exponential operator exchanges the valence electron with a core electron of the same spin orientation. The new approximation consists of replacing Eq. (7) by

$$V_{\text{xc}} \simeq V_c[1 - (a/Z_c^{2/3}e^{-r/r_2}] \equiv V_c + V_{\text{x2}}, \qquad (8)$$

where $a = \frac{5}{3}(2/2\pi)^{2/3} \simeq 1.018$, Z_c is the number of

core electrons, and

$$V_c = 2\sum_c \langle \varphi_c | |\vec{r} - \vec{r}_c|^{-1} | \varphi_c \rangle \qquad (9)$$

is the interelectronic Coulomb repulsion. The coefficient $aZ_c^{-2/3}$ is determined by comparing Coulomb and exchange energies of an electron gas of constant density in a spherical container. Adjustment of r_2 was made to match energies of the lowest states of a given symmetry. Results indicate that V_{x2} also represents the exchange better than V_{x0} (see Table II).
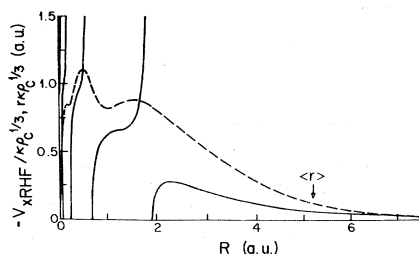
FIG. 1. *Ratio* of the effective local exchange determined from the radial Dirac wave functions (see text) to the statistical exchange term $-\varkappa\rho_c^{1/3}$ (solid line) for the $5s_{1/2}$ state of Rb I. Singularities occur at nodes in the large component P. The radial dependence of $r\varkappa\rho_c^{1/3}$ is also shown (dashed line) as is the average radius $\langle r \rangle$ of the $5s_{1/2}$ orbital (arrow).

V. DISCUSSION

The percentage errors given for the calculated ionization energies ϵ and the average radii $\langle r \rangle$ in Table II provide a direct measure of deficiencies in the local approximations to the exchange interaction between the valence and core electrons. The ionization energies ϵ are more sensitive to the inner regions of the potential, and the average radii $\langle r \rangle$, to the outer regions. (Since the single parameter in the local exchange potentials was adjusted to match the ionization energy of the lowest state of given symmetry to the RHF-CP value, the energy error for these states is zero).

When the Slater-type potential V_{x0} [Eq. (2)] is used, energies and radii seem to be typically about 1% in error. The ionization energies are uniformly too small and the average radii are too large, an indication that with the adjusted value of λ, V_{x0} tends to underestimate the exchange interaction near the origin and to overestimate it at large r. This is in accordance with conclusions drawn above from Fig. 1. The error in $\langle r \rangle$ is as large as 4.25% when V_{x0} is used for the $5s_{1/2}$ state of Ag, a state for which the error in ϵ has been adjusted to zero.

In contrast, errors arising from the use of the local potentials V_{x1} or V_{x2} are typically tenths of a percent or less. Also V_{x1} and V_{x2} follow the

form of the effective local exchange V_{xRHF} (except, of course, for the singularities of V_{xRHF}) more closely than does V_{x0} (see Fig. 1), and as a consequence their associated errors (Table II) do not display the strong systematic trends seen with V_{x0}. In no case studied are the errors with V_{x1} or V_{x2} as large as 1% and, except for the excited $s_{1/2}$ states of Ag (for which errors are comparable) and for a few i̇solated cases for which the errors in V_{x0} appear fortuitously small, errors with V_{x1} and V_{x2} are generally a factor of 2 or more smaller than the corresponding ones for V_{x0}. The root-mean-square errors for the calculations with V_{x0}, V_{x1}, and V_{x2} are 0.72, 0.13, and 0.17%, respectively, for energies and 1.34, 0.24, and 0.34%, respectively, for average radii.

Thus we have found two local approximations which appear significantly better able to represent true nonlocal exchange effects between valence and core electrons than the Slater-type term V_{x0} [Eq. (2)]. Oscillator strengths are rather less sensitive to the form of the exchange potential than are average radii and eigenenergies, but they too show some improvement when V_{x0} is replaced by V_{x1} or V_{x2}. Of course, V_{x1} and V_{x2} are both as simple to use as V_{x0} and, like V_{x0}, they each have one adjustable parameter.

The MP-CP calculations discussed here are identical to the RHF-CP ones *except* in the treatment of exchange. This is necessary in order to isolate effects arising from approximations of the exchange from other sources of error. Had less accurate densities been used, for example, errors arising from the densities might have compensated errors due to V_{x0}. Indeed, in calculations with Gombas-Szondy densities,[15] which tend to be too compact, V_{x0} has been found to give results somewhat closer to the RHF-CP values than when V_{x1} or V_{x2} is used.[16] However, this in no way alters our conclusions about the relative ability of V_{x0}, V_{x1}, and V_{x2} to represent the exchange interaction between valence and core electrons.

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