PHYSICAL REVIEW A

GENERAL PHYSICS

THIRD SERIES, VOLUME 24, NUMBER 2 AUGUST 1981

Nonadjustable local model potentials for the exchange interaction between valence and core electrons

J. Migdalek* and W. E. Baylis

Department of Physics, University of Windsor, Windsor, Ontario, Canada N9B 3P4

(Received 22 December 1980)

The ability of existing nonadjustable local-exchange approximations to represent interelectronic exchange is tested by comparing valence-electron energies and average radii in Rb and Ag as determined in two different approaches: a relativistic-model-potential approach and one employing the polarizable frozen-core relativistic Hartree-Fock method. The calculations are identical in these two approaches except for the treatment of exchange. Two approximations originally developed for electron-atom-scattering processes are found to be the most accurate. A new approximation based on the free-electron-gas model is also discussed.

I. INTRODUCTION

The accessibility of large and fast computing facilities has made relativistic Hartree-Fock (RHF) computations feasible and fairly popular. Nevertheless, there still exists a strong interest in simplifications of this procedure in calculations of the interaction between valence electrons and closed-shell cores, especially in molecular and solid-state applications. These simplifications are mainly based on two assumptions: (1) the possibility of separating "valence" and "core" electrons and, consequently, of reducing the many-electron problem to one involving only valence electrons, and (2) a local approximation for exchange.

If the electron density of the core is available, the resulting Coulomb potential is easily found, and this together with the local-exchange potential and a polarization potential may be used to create a model potential (MP). The only difference between relativistic computations using such a MP and relativistic polarizable frozen-core Hartree-Fock results arises from the treatment of exchange, which is nonlocal in the HF case but approximated by a local potential in the MP calculation. Therefore, the comparison of MP calculations with their corresponding frozen-core HF counterparts permits a direct evaluation of the local-exchange approximation employed in the MP approach. The authors have recently[1] taken advantage of this direct comparison in order to test the accuracy of *adjustable* local approximations for the exchange between valence and core electrons based on the Slater term[2] and to suggest two new adjustable local-exchange potentials. The purpose of this paper is to investigate the ability of existing local-exchange approximations with no adjustable parameters to represent the exchange between valence and core electrons for bound electron states in the energy range of 0.1 to 0.001 a.u. The use of MP's can provide valuable savings in computational time, particularly for lengthy calculations such as the electron-atom- or electron-molecule-scattering problems for which some of the local-exchange approximations have been introduced.[3] Their use is easily justified if the results are sufficiently accurate. It is the question of accuracy which we address.

Jaffe and Reinhardt[4] previously tested some of these potentials by comparing calculations of quantum defects of Rydberg states in alkalis (Na, K) with experiment. In contrast to Jaffe and Reinhardt's study, however, the present approach permits a direct and unambiguous evaluation of the error introduced into computations when the exact exchange interaction is replaced by different local approximations. Our study should complement a recent comparison[5] of exchange approximations in electron-molecule scattering.

II. LOCAL-EXCHANGE APPROXIMATIONS

A. Free-electron-gas approximations

The exchange potential for an electron in a free-electron gas is (atomic units $e=m=\hbar=1$ are used throughout)

$$V_{\text{exch}}=-2\kappa F(\eta)\rho^{1/3}, \tag{1}$$

where $\kappa=(3/\pi)^{1/3}$, ρ is the number density of electrons, and

$$F(\eta)=\frac{1}{2}+\frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| \tag{2}$$

$$\eta=(p/p_F), \tag{3}$$

where p is the single-electron momentum and p_F is the Fermi momentum of electron distribution, given by

$$p_F=\pi\kappa\rho^{1/3}. \tag{4}$$

If the potential of Eq. (1) is used to represent the sum of interelectronic and "self" exchange as in Hartree-Fock-Slater (HFS) calculations then ρ is the total electron density of the atom or ion and p_F is the Fermi momentum of the total electron distribution. Slater[2] replaced $F(\eta)$ by its average over the Fermi sphere, which is $\frac{3}{4}$. Gaspar,[6] Kohn and Sham,[7] and Cowan *et al.*[8] used an energy minimization procedure to obtain the alternative constant value $F(\eta)=\frac{1}{2}$. It is well established that the inclusion of self-exchange should, in principle, cancel the self-Coulombic repulsion. However, when Eq. (1) is used, this cancellation is by no means exact, and the use of self-exchange leads to the wrong asymptotic form of the potential energy and therefore requires an artificial "tail correction."

In MP applications these difficulties are avoided by using Eq. (1) to represent the interelectronic part of the exchange only. Here ρ is set equal to the core-electron density ρ_c and p_F is the Fermi momentum of the core-electron distribution. Thus, for a valence electron interacting with a core, $p>p_F$ and consequently $\eta>1$ and $F(\eta)<\frac{1}{2}$. There is now ample evidence that the potential given by Eqs. (1)–(4), in which constant values are adopted for $F(\eta)$ in accordance to suggestions made by Slater or by Gaspar and by Kohn and Sham, does not satisfactorily represent the interelectronic exchange.[1,4] Nevertheless, the potential from Eqs. (1)–(4) can still be successfully used for interelectronic exchange if $F(\eta)$ is treated as an adjustable parameter.[10] The values of $F(\eta)$, adjusted to match experimental ionization energies, are then much lower than those suggested by Slater or by Gaspar and by Kohn and Sham; for Rb and Ag they are typically 0.15–0.25.[1,11]

Kohn and Sham,[7] Yonei,[12] and Liberman[13] suggested an approach in which the semiclassical approximation is used for p in Eq. (2),

$$p=\{2[E-V(r)]\}^{1/2}, \tag{5}$$

where $E<0$ is the energy of valence electron and $V(r)<0$ is the effective potential seen by this electron.

The potential given by Eqs. (1)–(5) may be used for interelectronic exchange by setting ρ equal to the core-electron density. The exchange-potential contribution to the effective potential $V(r)$ in Eq. (5) is omitted to avoid the need for a self-consistent procedure. The potential given by Eqs. (1)–(5) will be further referred to as free-electron-gas exchange (FEGE). The ratio p/p_F should increase from about unity at $r=0$ to much larger values at large r and, consequently, $F(\eta)$ ($=\frac{1}{2}$ at $\eta=1$) will decrease rapidly with increasing η or r. It should be stressed here that this behavior of $F(\eta)$ is completely different from that occurring when the potential [Eqs. (1)–(5)] is used to represent the sum of the interelectronic and self-exchange and ρ is the total atom electron density.[14]

As r approaches the classical turning point r_c, $p\to 0$, $\eta\to 0$, and $F(\eta)$ rises sharply and unphysically to about unity. Hence, $F(\eta)$ should be cut before the classical turning point and patched with a decreasing function of r. On the basis of our previous experience[1] the form $F(\eta)=\frac{1}{2}e^{-r/r_1}$ is used for $r\geq r_c$, where r_1 is chosen so as to match $F(\eta)$ at a point before r_c.

An alternative approach has been developed by Hara[15] for electron-atom and electron-molecule scattering. It is based on the assumption that the valence electron and core electrons see the same effective field $V(r)$, which can be approximated by the Fermi energy of the core and its ionization potential I. This leads to the expression for the single electron momentum p:

$$p=[2(E+I)+p_F^2]^{1/2}. \tag{6}$$

This approximation implies that the valence electron has kinetic energy $E+I$ at large r, rather than E; however, Hara suggested that this inconsistency may not be important since the exchange potential Eq. (1) is small in the large-r region. Equation (6) together with Eqs. (1)–(4) will be referred to as Hara free-electron-gas exchange (HFEGE).

The assumption that valence and core electrons are affected by the same effective potential $V(r)$ may also be utilized in a way that leads to a form of local-exchange potential different from that of Hara. We determine the Fermi momentum of the core rather than the effective potential $V(r)$:

$$p_F=\{2[-I-V(r)]\}^{1/2}\,. \tag{7}$$

The method which uses Eq. (7) together with Eqs. (1)–(3) and Eq. (5) will be called classically approximated free-electron-gas exchange (CAFEGE). For $r \gtrsim r_{cc}$, where r_{cc} is the classical turning point for the core determined by Eq. (7), the exchange potential is set to zero.

In order to avoid the self-consistent procedure connected with the appearance of the exchange term in the effective potential $V(r)$ in Eq. (5), Yonei[12] has also suggested an approach in which the single-electron momentum p is approximated by the Fermi momentum of the total atom electron distribution:

$$p \approx p_F^{\text{atom}} \tag{8}$$

and

$$\eta=\frac{p}{p_F^{\text{core}}} \simeq \frac{p_F^{\text{atom}}}{p_F^{\text{core}}}=\left(\frac{\rho_a}{\rho_c}\right)^{1/3}=\left(1+\frac{\rho_v}{\rho_c}\right)^{1/3}, \tag{9}$$

where ρ_v is the density of the valence electron.

The approximation using Eqs. (9) and (1) and (2) will be referred to as Yonei free-electron-gas exchange (YFEGE). The values of ρ_v are taken from the previous iteration of MP calculations.

B. Semiclassical exchange

Recently, Riley and Truhlar,[16] used another approximation to exchange in electron-atom scattering. On the basis of the Poisson equation, they suggested the following form of the local potential:

$$V_{\text{exch}}=\tfrac{1}{2}[E-V_s(r)]-\tfrac{1}{2}\{[E-V_s(r)]^2+\beta^2\}^{1/2}, \tag{10}$$

where for cores with doubly occupied spatial orbitals

$$\beta^2=4\pi\rho_c\,, \tag{11}$$

ρ_c is the electron density of the core, and V_s is the sum of the Coulomb and polarization potentials.

The exchange potential represented by Eqs. (10) and (11) called by its authors the "semiclassical exchange" (SCE) potential. (A local approximation of identical form was derived earlier in a different manner by Furness and McCarthy.[17]) For bound states ($E<0$) as r approaches the classical turning point r_c, V_{exch} becomes equal to $-\frac{1}{2}\beta$, whereas for $r \gg r_c$ it increases in magnitude and tends to E. Therefore, the potential of Eq. (10) must be cut shortly before the classical turning point and replaced by its form at the classical turning point, namely, $-\frac{1}{2}\beta$, which tends to zero for large r.

III. CALCULATIONS

The local exchange approximations described in Sec. II are tested by comparing relativistic MP and HF calculations, which differ only in their treatment of the exchange interaction. Relativistic HF calculations (RHF+CP) are carried out with a version of the Desclaux[18] program modified to include core-polarization effects[19] through the addition of a polarization potential

$$V_{\text{pol}}=-\tfrac{1}{2}\alpha r^2(r^2+r_0^2)^{-3}\,, \tag{12}$$

where α is the dipole polarizability of the core as calculated by Fraga *et al.*[20] and r_0 is the cutoff radius which is adjusted in RHF+CP calculations to reproduce the experimental ground-state ionization energy. The MP calculations with core polarization (MP+CP) employ polarization potentials and ionlike core densities identical to these found or used in the RHF+CP case. The computer code for the MP calculations is, except for the different core densities and exchange potential, the same as developed and described by one of us previously[10]. The eigenvalue of the outermost electron of the ionlike core

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

Spectrum	I[a]	α[b]	State	r_0[c]
Rb I	0.997 637	11.15	$s_{1/2}$	1.478
			$p_{1/2}$	1.581
			$p_{3/2}$	1.596
			$d_{3/2}$	1.767
			$d_{5/2}$	1.776
Ag I	0.800145	10.07	$s_{1/2}$	1.326
			$p_{1/2}$	1.279
			$p_{3/2}$	1.265
			$d_{3/2}$	1.377
			$d_{5/2}$	1.392

[a] The eigenvalue ϵ of the outermost electron in Rb^+ and Ag^+ calculated with the relativistic Hartree-Fock method (RHF) without core polarization was employed as the ionization potential of the core in V^{HFEGE} and V^{CAFEGE}. (Koopmans's theorem was assumed to be valid: $I=-\epsilon$ in the frozen-core calculations.)

[b] Dipole polarizabilities of the parent-ion cores are taken from Fraga *et al.* (Ref. 20).

[c] The cutoff radius in the polarization potential [Eq. (12)] is adjusted (Ref. 11) in relativistic Hartree-Fock calculations to give experimental ionization energies (Ref. 21).

TABLE II. Percent errors in one-electron energies ϵ of Rb and Ag as calculated by the model-potential method (MP) without exchange and with five different local *ab initio* approximations to the exchange interaction between the valence electron and the parent-ion core as compared to frozen-core relativistic Hartree-Fock results (RHF). All calculations include core polarization (CP) and are otherwise identical except for their treatment of exchange.

		$100\times(\epsilon^{\mathrm{MC+CP}}-\epsilon^{\mathrm{RHF+CP}})/\epsilon^{\mathrm{RHF+CP}}$					
State	$\epsilon^{\mathrm{RHF+CP}}$ (a.u.)	No. exchange	V^{SCE}	V^{FEGE}	V^{HFEGE}	V^{CAFEGE}	V^{YFEGE}
Rb $ns_{1/2}$							
$n=$ 5	0.153 514	−17.3	0.34	54.6	−2.97	−6.16	19.6
6	0.061 791	−10.7	−0.77	19.3	−1.56	−3.46	13.8
7	0.033 625	−7.92	−0.67	13.1	−1.10	−2.48	9.85
9	0.014 543	−5.25	−0.47	8.20	−0.69	−1.60	6.31
25	0.000 990 12	−3.73	−2.19	0.32	−2.28	−2.55	−0.17
Rb $np_{1/2}$							
$n=$ 5	0.096 197	−16.6	−1.66	19.4	−1.70	−4.06	13.0
6	0.045 429	−11.3	−1.23	12.1	−1.09	−2.66	11.1
7	0.026 665	−8.73	−0.96	9.06	−0.81	−2.01	9.09
9	0.012 442	−6.02	−0.66	6.06	−0.54	−1.35	6.39
20	0.001 646 2	−3.80	−1.66	0.83	−1.66	−1.96	1.00
Rb $np_{3/2}$							
$n=$ 5	0.095 114	−17.3	−1.93	18.4	−1.98	−4.55	12.2
6	0.045 076	−11.8	−1.40	11.7	−1.27	−2.98	10.5
7	0.026 505	−9.12	−1.08	8.74	−0.96	−2.25	8.67
9	0.012 391	−6.30	−0.74	5.86	−0.65	−1.53	6.15
20	0.001 644 4	−3.87	−1.67	0.83	−1.61	−1.98	1.00
Rb nd							
$n=$ 5	0.036 405	−11.0	−2.29	49.6	−6.67	−9.80	31.0
6	0.022 804	−9.59	−2.07	33.8	−5.70	−8.52	21.1
7	0.015 545	−8.30	−1.81	25.9	−4.85	−7.35	16.2
9	0.008 519	−6.43	−1.39	17.7	−3.67	−5.66	11.2
Rb $nd_{5/2}$							
$n=$ 5	0.036 392	−11.0	−2.50	49.5	−6.79	−9.83	30.6
6	0.022 794	−9.59	−2.25	33.8	−5.80	−8.53	20.8
7	0.015 538	−8.30	−1.95	25.8	−4.93	−7.36	16.0
9	0.008 515	−6.42	−1.49	17.7	−3.73	−5.66	11.1
Ag $ns_{1/2}$							
$n=$ 5	0.278 419	−27.6	21.7	167.5	5.19	−13.2	34.7
6	0.084 339	−13.4	2.46	32.1	1.44	−4.93	14.3
7	0.041 926	−9.37	1.39	20.1	0.91	−3.26	10.1
9	0.016 750	−5.95	0.79	11.8	0.55	−1.99	6.66
25	0.001 033 6	−3.81	−1.87	1.08	−1.96	−2.68	−0.03
Ag $np_{1/2}$							
$n=$ 5	0.143 771	−19 1	5.90	239.9	−0.11	−9.74	37.5
6	0.058 252	−11.2	1.34	33.9	0.05	−4.93	17.4
7	0.032 111	−8.30	0.77	22.2	0.06	−3.47	12.0
9	0.014 094	−5.52	0.43	13.5	0.06	−2.23	7.65
20	0.001 724 1	−3.39	−1.18	3.30	−1.29	−2.11	1.58
Ag np							
$n=$ 5	0.139 576	−18.5	4.56	233.0	−0.68	−9.13	34.3
6	0.057 303	−11.1	0.97	32.6	−0.22	−4.73	17.2
7	0.031 729	−8.20	0.52	21.4	−0.14	−3.35	11.8
9	0.013 983	−5.47	0.28	13.1	−0.06	−2.16	7.55
20	0.001 720 0	−3.33	−1.17	3.22	−1.28	−2.04	1.55
Ag $nd_{3/2}$							
$n=$ 5	0.056 319	−39.8	−1.11	3.85	−0.58	−1.39	5.77
6	0.031 450	−31.7	−1.00	3.65	−0.51	−1.21	6.10

TABLE II. (*Continued*).

State	$\epsilon^{\mathrm{RHF+CP}}$ (a.u.)	No exchange	V^{SCE}	V^{FEGE}	V^{HFEGE}	V^{CAFEGE}	V^{YFEGE}
		$100\times(\epsilon^{\mathrm{MP+CP}}-\epsilon^{\mathrm{RHF+CP}})/\epsilon^{\mathrm{RHF+CP}}$					
Ag $nd_{3/2}$							
$n=$ 7	0.020 076	−26.3	−0.84	3.17	−0.42	−1.02	5.80
9	0.010 224	−19.7	−0.62	2.43	−0.30	−0.74	4.97
Ag $nd_{5/2}$							
$n=$ 5	0.056 221	−40.0	−1.24	3.83	−0.67	−1.60	5.41
6	0.031 400	−31.9	−1.10	3.63	−0.58	−1.38	5.88
7	0.020 049	−26.5	−0.93	3.15	−0.49	−1.16	5.63
9	0.010 213	−19.8	−0.68	2.40	−0.35	−0.85	4.80

TABLE III. Percent errors in average valence-shell radii $\langle r\rangle$ of Rb and Ag as calculated by the model-potential method (MP) without exchange and with five different local *ab initio* approximations to the exchange interaction between the valence electron and the parent-ion core as compared to frozen-core relativistic Hartree-Fock results (RHF). All calculations include core polarization (CP) and are otherwise identical except for their treatment of exchange.

State	$\langle r\rangle^{\mathrm{RHF+CP}}$ (a.u.)	No exchange	V^{SCE}	V^{FEGE}	V^{HFEGE}	V^{CAFEGE}	V^{YFEGE}
		$100\times(\langle r\rangle^{\mathrm{MC+CP}}-\langle r\rangle^{\mathrm{RHF+CP}})/\langle r\rangle^{\mathrm{RHF+CP}}$					
Rb $ns_{1/2}$							
$n=$ 5	5.182	−18.7	−0.58	−28.8	2.16	5.54	−15.4
6	12.328	11.5	0.58	−16.0	1.31	3.28	−11.2
7	22.445	8.45	0.56	−11.6	0.98	2.43	−8.54
9	51.666	5.52	0.43	−7.61	0.67	1.57	−5.81
25	867.207	−5.83	−6.46	−8.62	−6.69	−6.52	−8.83
Rb $np_{1/2}$							
$n=$ 5	7.178	20.7	1.42	−19.1	1.52	4.21	−13.3
6	15.778	13.1	1.13	−11.8	1.00	2.70	−10.2
7	27.331	9.73	0.93	−8.78	0.79	2.06	−8.34
9	59.424	6.54	0.61	−5.88	0.54	1.38	−6.04
20	489.137	3.06	1.18	−2.16	0.26	0.73	−2.32
Rb $np_{3/2}$							
$n=$ 5	7.273	21.6	1.69	−18.2	1.80	4.69	−12.5
6	15.908	13.7	1.33	−11.4	1.22	3.06	−9.77
7	27.504	10.2	1.04	−8.49	0.91	2.29	−8.01
9	59.676	6.73	0.75	−5.68	0.61	1.55	−5.91
20	488.896	3.26	0.87	−1.63	0.31	1.10	−1.91
Rb $nd_{3/2}$							
$n=$ 5	17.003	17.9	3.07	−35.5	9.92	15.6	−23.3
6	29.437	13.1	2.39	−26.1	7.16	11.4	−17.1
7	44.889	10.4	1.99	−21.0	5.68	9.00	−13.7
9	84.815	7.42	1.45	−15.2	4.07	6.42	−9.99
Rb $nd_{5/2}$							
$n=$ 5	17.019	17.9	3.35	−35.4	10.1	15.7	−23.1
6	29.461	13.1	2.59	−26.1	7.24	11.3	−17.0
7	44.918	10.4	2.14	−20.9	5.77	9.00	−13.6
9	84.848	7.43	1.54	−15.3	4.14	6.39	−9.95
Ag $ns_{1/2}$							
$n=$ 5	3.174	26.2	−7.15	−30.7	−4.51	7.91	−15.3
6	9.130	14.2	−2.31	−22.9	−1.62	4.29	−11.8
7	18.052	9.94	−1.38	−16.4	−0.99	3.09	−8.96
9	44.879	6.20	−0.78	−10.5	−0.56	1.95	−6.23
25	827.987	−4.04	−5.93	−8.40	−6.41	−5.76	−7.98

TABLE III. (*Continued*).

State	$\langle r\rangle^{\mathrm{RHF+CP}}$ (a.u.)	$100\times(\langle r\rangle^{\mathrm{MC+CP}}-\langle r\rangle^{\mathrm{RHF+CP}})/\langle r\rangle^{\mathrm{RHF+CP}}$					
		No exchange	V^{SCE}	V^{FEGE}	V^{HFEGE}	V^{CAFEGE}	V^{YFEGE}
Ag $np_{1/2}$							
$n=$ 5	4.598	24.9	−5.00	−45.4	−0.98	10.0	−21.6
6	12.131	13.0	−1.43	−25.6	−0.39	4.92	−14.7
7	22.550	9.20	−0.81	−18.4	−0.20	3.50	−10.6
9	52.348	5.87	−0.43	−12.0	−0.086	2.27	−7.09
20	463.676	2.65	0.25	−4.15	0.47	1.56	−2.26
Ag $np_{3/2}$							
$n=$ 5	4.744	24.1	−4.11	−45.5	−0.34	9.53	−21.5
6	12.341	12.8	−1.10	−24.9	−0.11	4.74	−14.0
7	22.829	9.09	−0.60	−17.9	−0.0088	3.39	−10.4
9	52.766	5.86	−0.30	−11.7	0.049	2.16	−7.04
20	464.143	2.87	0.81	−3.91	0.92	1.78	−2.36
Ag $nd_{3/2}$							
$n=$ 5	10.380	80.1	1.74	−6.82	0.89	2.20	−9.01
6	20.920	50.6	1.24	−4.92	0.63	1.53	−7.63
7	34.425	37.5	0.97	−3.83	0.49	1.19	−6.81
9	70.419	25.1	0.68	−2.64	0.31	0.84	−5.02
Ag $nd_{5/2}$							
$n=$ 5	10.411	80.9	1.92	−6.76	1.00	2.49	−8.93
6	20.964	51.1	1.35	−4.89	0.72	1.73	−7.21
7	34.481	38.0	1.06	−3.79	0.53	1.32	−6.18
9	70.435	25.5	0.81	−2.53	0.41	0.98	−4.82

is used as the ionization potential I of the core, which appears in the HFEGE and CAFEGE local approximations. The values of parameters used are summarized in Table I. The MP calculations, with exchange interaction omitted, are also performed to estimate the influence of exchange on calculated quantities. The atoms chosen for computation, Rb and Ag as in our previous study,[1] are fairly typical representatives of cases where statistical approximation of the interelectronic exchange is thought to be appropriate. As in our previous paper[1] the calculated one-electron energies of valence electrons and average radii of the valence orbitals are compared. These appear to provide sensitive monitors of the overall potential. The energy is usually more sensitive to small-r region, whereas the average radius is more affected by the potential at large r.

IV. DISCUSSION

The percentage errors for the calculated one-electron energies and the average radii $\langle r\rangle$ of the valence orbitals are given in Tables II and III, respectively. They provide a direct measure of deficiencies in the local approximations to the exchange interaction between valence and core electrons. The MP calculations performed without exchange demonstrate that the influence of this interaction may reach in some cases ($5d_{3/2,5/2}$ states in Ag) as much as 40% for one-electron energies and even 80% for mean radii. It is also seen that although the contribution of exchange decreases with increasing principle quantum number n, it still amounts to about 3–4% even for states with $n=20$–25 and is thus by no means negligible. The FEGE approximation strongly overestimates the exchange, particularly for low but also for medium n values, whereas it appears to be fairly good approximation for high-lying states ($n=20$–25). The same can be said about the YFEGE approximation, though it overestimates the exchange to smaller extent than FEGE. The newly suggested CAFEGE approximation underestimates the exchange, though it brings a considerable improvement over the results obtained without exchange at all. The SCE approximation appears to be very successful, except for the ground state of Ag. It mostly underestimates the exchange for Rb, but overestimates it for half of the states of Ag. Its error in most cases (except for lowest s and p states in Ag) does not exceed 3%. A similarly good overall agreement with RHF + CP results is achieved with the HFEGE approximation. It mostly underestimates the exchange, but for some states of Ag($ns_{1/2}$, $np_{1/2}$) a slight overestimation has also been observed. The HFEGE approach gives worse results than SCE for s and d states of Rb, but is better for all states of Ag. The root-mean-square errors for calculations with FEGE, YFEGE, CAFEGE, SCE, and HFEGE approximations are 58.8%, 15.1%, 5.00%, 3.64%, and 2.58%, respectively, for energies and 18.8%, 11.6%, 5.86%, 2.36%, and 3.42%, respectively, for average radii.

For comparison, the rms error introduced by completely neglecting exchange is 16.1% for energies and 24.9% for average radii. It may be seen from comparison of rms errors that FEGE overestimates the exchange more strongly in the small-r region (which contributes the most to one-electron energies) than at large r (the main contribution into the average radii). A similar trend may be seen, though to a smaller degree, for YFEGE. For the remaining approximations, however, the errors introduced are comparable in both one-electron energies and average radii.

We can conclude from this study that the most successful nonadjustable local approximations for exchange interaction between valence and core electrons are the semiclassical exchange of Furness and McCarthy[17] and of Riley and Truhlar[16] (SCE) and the free-electron-gas exchange of Hara[18] (HFEGE), which were both developed to treat the exchange for electron-atom-scattering processes. This confirms the conclusions of Jaffe and Reinhardt[4] based on comparisons of the calculated quantum defects of Rydberg states with experiment. However, for highly excited states with ionization energies below 0.002 a.u. the error rises sharply for the SCE and HFEGE approximations (see Tables II and III) and in this case the FEGE approximation (SOFEGE in the paper of Jaffe and Reinhardt[4]) appears to be at least as good and frequently much better. This has not been mentioned by Jaffe and Reinhardt, who found FEGE generally too attractive. Unfortunately, they did not include in their paper the results obtained with this approximation. As discussed in Sec. II the Slater and Gaspar-Kohn-Sham local-exchange potentials, which have also been found unsuccessful by Jaffe and Reinhardt, are quite useless for the approximation of the exchange interaction between valence and core electrons, since they assume a constant value of the function $F(\eta)$ ($=\frac{3}{4}$ or $\frac{1}{2}$, respectively), whereas the interelectronic exchange, (in contrast to the sum of the interelectronic and self-exchange interaction) requires $F(\eta)$ smaller than $\frac{1}{2}$ and decreasing rapidly at large r.

ACKNOWLEDGMENT

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

---

*On leave from the Institute of Physics, Jagellonian University, 30-059 Krakow, Poland.

[1] J. Migdalek and W. E. Baylis, Phys. Rev. A 22, 22 (1980).

[2] J. C. Slater, Phys. Rev. 81, 385 (1951).

[3] B. H. Bransden, M. R. C. McDowell, C. J. Noble, and T. Scott, J. Phys. B. 9, 1301 (1976).

[4] C. Jaffe and W. P. Reinhardt, J. Chem. Phys. 65, 4321 (1976).

[5] M. A. Morrison and L. A. Collins, Phys. Rev. A 23, 127 (1981).

[6] R. Gaspar, Acta Phys. Acad. Sci. Hung. 3, 263 (1954).

[7] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[8] R. D. Cowan, A. C. Larson, D. Liberman, J. B. Mann, and J. Waber, Phys. Rev. 144, 5 (1966).

[9] R. Latter, Phys. Rev. 99, 510 (1955).

[10] J. Migdalek, Can. J. Phys. 54, 118 (1976).

[11] J. Migdalek and W. E. Baylis, Can. J. Phys. 57, 1708 (1979).

[12] K. Yonei, J. Phys. Soc. Jpn. 22, 1127 (1967).

[13] D. A. Liberman, Phys. Rev. 171, 1 (1968).

[14] J. C. Slater, T. M. Wilson, and J. M. Wood, Phys. Rev. 179, 28 (1969).

[15] S. Hara, J. Phys. Soc. Jpn. 22, 710 (1967).

[16] M. E. Riley and D. G. Truhlar, J. Chem. Phys. 64, 2182 (1975).

[17] J. B. Furness and I. E. McCarthy, J. Phys. B 6, 2280 (1973).

[18] J. P. Desclaux, Comput. Phys. Commun. 9, 31 (1975).

[19] J. Migdalek and W. E. Baylis, J. Phys. B 11, L497 (1978); 12, 1113 (1979); J. Quant. Spectrosc. Radiat. Transfer 22, 113 (1979).

[20] S. Fraga, J. Karwowski, and K. M. S. Saxena, *Handbook of Atomic Data* (Elsevier, Amsterdam, 1976).

[21] I. Johansson, Ark. Fys. 20, 135 (1961); C. E. Moore, *Atomic Energy Levels*, National Stand. Ref. Data Ser. No. 35 (National Bureau of Standards, Washington, D. C., 1971).