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Nonadjustable exchange-correlation model for electron scattering from closed-shell atoms and molecules

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A nonadjustable-model potential is proposed for electron scattering that includes both electron exchange and correlation effects in a hybridization of local electron-gas theory and the long-range polarization. The model potential energy function consists of the sum of the energy-dependent electron-gas exchange potential (Hara version) and the energy-independent electron-gas correlation potential smoothly joined onto the long-range polarization interaction. Illustrative calculations of elastic scattering phase shifts and cross sections are described for the rare-gas atoms, where reasonable agreement with accurate calculations suggests usefulness of the model for more complex systems.

I. INTRODUCTION

The theoretical complexity of the electronic structure or electron-scattering dynamics of atoms and molecules is due to electron exchange and correlation effects.[1,2] Electron-exchange effects are due to the Pauli exclusion principle and the consequence that the total wave function of the system must be antisymmetric with respect to the interchange of the coordinates (spatial and spin) of any two electrons. Viewed another way, the requirement is that the probability that two electrons of like spin occupy the same location in space is zero, i.e., each electron is surrounded by a "Fermi hole." Thus the repulsive interaction between electrons of like spins is suppressed relative to that between electrons of unlike spins in any determination of the bound-state energy or electron-scattering properties of an atomic or molecular system. This "exchange" aspect of the problem is fully accounted for in the Hartree-Fock formalism, often referred to as "static-exchange" theory in the case of electron scattering. While the static-exchange method is straightforward in principle, it nevertheless requires the handling of nonlocal interactions, and application to large systems can be very tedious. Thus a variety of exchange approximations has been devised to permit the study of large molecules, clusters, surfaces, and other forms of condensed matter.[3,4] The majority of such approaches is based on the local density approximation (LDA), where it is assumed that electron-exchange effects can be adequately represented by an exchange potential energy function

$$V_{\rm exch}(\vec{r})=2\mathscr{E}_x[\rho(\vec{r})]\ , \tag{1}$$

which depends on electron coordinates $\vec{r}$ only though the *local* electron density $\rho(\vec{r})$ appearing in the exchange energy density $\mathscr{E}_x[\rho]$. The adequacy of Eq. (1) is, of course, not guaranteed by the fundamental theorem of Hohenberg and Kohn[5]; however, the HK theory does establish the particle density as a fundamentally significant variable on which to base such an approximation.[6,7]

Electron correlation generally refers to everything left out of a Hartree-Fock (or static-exchange) calculation. The physical picture of electron correlation is straightforward. In the Hartree-Fock approach each electron is assumed to move in the *average* self-consistent field (SCF) of the other electrons, taking into account only the Coulomb energy and the Pauli exclusion principle. Correlation is the correction of this *average* interaction to allow electrons to avoid one another, not only "on the average" but in every region of configuration space. Thus in addition to the "Fermi hole," each electron surrounds itself with a "Coulomb hole" from which other electrons are excluded. When a single electron is removed sufficiently far from the other electrons, e.g., one bound or continuum electron outside a closed shell, correlation takes the form of charge polarization of the inner-electron distribution (plus nucleus), resulting in an induced dipole moment. Thus in the asymptotic limit, a static correlation (polarization) potential energy may be identified of the form (atomic units will be used throughout)

$$V_{\rm pol}(r) \underset{r\to\infty}{\sim} -\frac{\alpha_d}{2r^4}\ , \tag{2}$$

where α_d is the electric dipole polarizability of the inner charge distribution (i.e., target atom or molecule in the case of electron scattering). Unfortunately, Eq. (2) applies only in the asymptotic limit and its proper form at smaller values of r is not simple and, in general, not known. In bound-state applications, correlation effects may be treated using methods based on perturbation theory or on the variational principle; still it is a formidable computational problem to obtain accurate results for complex systems. In continuum applications, the problem is even more difficult. While a number of impressive theoretical treatments of correlation in electron-atom and electron-molecule scattering and photoionization can be classified as *ab initio*, application to electron scattering from large molecules, clusters, or surfaces is simply out of reach of present-day computer capability.[4] Even the polarized-orbital method of Temkin[8] is difficult to apply to large nonspherical systems. The approach of most workers has been to employ some form of cut-off polarization potential having the asymptotic form of Eq. (2), where a few adjustable parameters control the manner in which the potential is cut off at small distances.[3,4] In some cases, the parameters are chosen semiempirically to reproduce an observed feature in the cross section, e.g., the position of a shape resonance. In other applications, "reasonable" choices of the cutoff are made based on the "size" of the target. Often, qualitatively accurate results are obtained using these methods; however the approach is unsatisfactory.

The purpose of this paper is to report on a simple model that does not involve semiempirical adjustment of parameters or guesswork. The approach represents nothing more than a hybridization of free-electron-gas (FEG) theory and the long-range polarization interaction, somewhat along the lines of Cohen and Pack[9] in their modification of the Gordon-Kim theory[10] of atom-atom interactions to include the long-range van der Waals contribution. Our approach is to adopt Hara's modification[11] of the free-electron exchange potential and to include correlation effects by smoothly joining the local FEG correlation energy[12] onto the long-range polarization energy of Eq. (2) where the two cross. Thus one requires only the electron density and polarizability of the target. We report here applications to elastic scattering from the rare gases He, Ne, Ar, Kr, and Xe since these atoms provide a range of electron densities and corresponding electron-gas characteristics. This sequence seemed the best choice to use in testing a model that we hope will be useful in describing more complex systems. Moreover, theoretical and experimental results are available for comparison. The approach described in this paper is similar, at least in spirit, to that used by Armstrong *et al.*[13] in their recent studies of exchange-correlation potentials in multichannel atomic quantum-defect calculations. However, the choice of exchange and correlation potentials is quite different. Ritchie *et al.*[14] and Migdalek and Baylis[15] have recently employed local exchange models in *e*-ion scattering and photoionization studies.

The organization of the paper is as follows. In Sec. II, the forms of the exchange and correlation potentials are described. In Sec. III the application to elastic electron scattering from rare-gas atoms is discussed and comparisons given with other theory as well as with experimental measurements.

II. EXCHANGE AND CORRELATION APPROXIMATIONS

The simplest and perhaps most widely used exchange potential employed in bound-state applications is the so-called "$X\alpha$ potential"

$$V_{X\alpha}(\vec{r}) = -(3\alpha/2\pi)[3\pi^2\rho(\vec{r})]^{1/3} , \tag{3}$$

where the parameter α (not to be confused with the polarizability) is chosen in a variety of ways.[16] Slater's original derivation of Eq. (2), based on treating the electrons as a free-electron gas and averaging the exchange energy over the Fermi sphere, gave $\alpha=1$. Gaspar,[17] Kohn and Sham,[6,7] and Cowan *et al.*[18] found that the smaller value $\alpha=\frac{2}{3}$ was consistent with the variational principle. In applications to atoms where α is chosen so as to yield a total ground-state energy in closest agreement with Hartree-Fock calculations, values in the range $0.7 \lesssim \alpha \lesssim 1.0$ have been obtained,[19] where $\alpha \simeq 0.7$ applies to most atoms in the periodic table. Analytical expressions have been derived for α in terms of the *number* of electrons in the atom of a given spin[20]; the agreement with Hartree-Fock energies and atomic orbitals is reasonably good.[21] Efforts have been made to extend these studies to correlation as well.[22]

In the case of elastic electron scattering from atoms or molecules, the $X\alpha$ exchange potential of Eq. (3) is less appropriate.[3,23] The continuum electron is not simply a representative electron in the Fermi sea and the characteristics of its wave function are quite different, especially at large r, from those of the bound electrons. Two approaches have been fairly successful: The semiclassical exchange (SCE) approximation of Riley and Truhlar[23] and the Hara free-electron-gas exchange (HFEG) approximation.[11] The SCE approach has the advantage that it generalizes in a natural way to open-shell targets and to spin coupling interactions that occur in spin-forbidden inelastic scattering. The modified FEG potential of Hara is based on the FEG exchange potential[24]

$$V_{\text{FEG}}(\vec{r}) = -\frac{2}{\pi}K_F F[\eta(\vec{r})] , \tag{4}$$

where

$$F[\eta]=\frac{1}{2}+\frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| \tag{5}$$

with

$$\eta(\vec{r})=K(\vec{r})/K_F(\vec{r}) \tag{6}$$

defined in terms of the "local momentum" $K(\vec{r})$ of the electron under consideration and the "local Fermi momentum"

$$K_F(\vec{r})=[3\pi^2\rho(\vec{r})]^{1/3}\ . \tag{7}$$

The assumptions made in applying Eq. (4) to an atom or molecule are primarily that one can appropriately partition the electron configuration space into small cells, each large enough so that the bound electrons can be represented as an electron gas obeying Fermi-Dirac statistics, yet small enough so that the electrons can be considered *free* inside a cell, i.e., a local momentum $K(\vec{r})$ and Fermi momentum $K_F(\vec{r})$ can be defined. The FEG potential of Eq. (4) is a starting point in Slater's derivation[16] of the $X\alpha$ potential in Eq. (3). This form can be derived by replacing the continuum orbitals in the ordinary two-electron exchange integral by appropriately normalized plane waves. If the functional $F[\eta]$ is averaged over the Fermi sphere, one obtains Eq. (3) with Slater's value of $\alpha=1$. Simply evaluating $F[\eta]$ at the Fermi surface $K=K_F$ yields $F[1]=\frac{1}{2}$ and $\alpha=\frac{2}{3}$ in Eq. (3). Hara's modification (HFEG)[11] of the FEG potential consists of shifting the zero of the energy, and hence local momentum $K(\vec{r})$ of the projectile electron so that it is consistent with that of the Fermi energy; thus Hara defines the local momentum $K(\vec{r})$ by

$$K(\vec{r})^2=K_F(\vec{r})^2+2I+k^2\ , \tag{8}$$

where I is the ionization potential of the target atom or molecule and $k^2/2$ is the incident kinetic energy of the projectile electron. In applications of the HFEG method to electron-molecule scattering[3,4,25,26] it has been found that the resulting continuum orbitals often are nearly orthogonal to the occupied bound-state molecular orbitals used in the calculation of the electron density. In all cases, the results were found to be improved by enforcing orthogonality via Lagrange multipliers during the calculation of the scattering wave function.[26] The HFEG approximation to exchange has also been found to work well in calculations of energies of valence states[15] of atoms and photoionization.[14,27] In the present study the HFEG exchange approximation is adopted.

The correlation problem in the free-electron gas has been a formidable challenge to the theory. The results of detailed calculations of correlation energy density for different ranges of electron-gas density can be represented by the relatively simple analytic fit[12,9,10]

$$2\mathscr{E}_c[\rho]\equiv\begin{cases}0.0622\ln r_s-0.096+0.018r_s\ln r_s-0.02r_s, & r_s\le 0.7\\ -0.1231+0.03796\ln r_s, & 0.7<r_s\le 10\\ -0.876r_s^{-1}+2.65r_s^{-3/2}-2.8r_s^{-2}-0.8r_s^{-5/2}, & 10\le r_s\end{cases} \tag{9}$$

where

$$r_s=(3/4\pi\rho)^{1/3}\ . \tag{10}$$

Thus assuming that the FEG correlation energy of Eq. (9) can be interpreted as a *local* correlation potential energy for the electron-target interaction, we define a short-range correlation potential[28]

$$V_c^{\rm SR}(\vec{r})\equiv 2\mathscr{E}_c[\rho(\vec{r})]\ . \tag{11}$$

This approximation to correlation clearly fails when the electron is beyond the outer edge of the atom or molecule since the electron-gas approximation makes no allowance for polarization of the target by the projectile electron. Thus a long-range correlation potential is simply defined as the polarization energy

$$V_c^{\rm LR}(\vec{r})\equiv V_{\rm pol}(r)=-\frac{\alpha_d}{2r^4}\ , \tag{12}$$

where α_d is the electric dipole polarizability of the target atom or molecule. The full correlation potential, then, is obtained by continuously joining the short- and long-range forms at the point r_c where the two cross thus obtaining

$$V_c(\vec{r})=\begin{cases}V_c^{\rm SR}(\vec{r}), & r\le r_c\\ V_c^{\rm LR}(\vec{r}), & r>r_c\end{cases}\ . \tag{13}$$

This is the simplest prescription for joining the electron-gas and polarization potentials and though *ad hoc*, it is unambiguous and free of adjustable parameters. It should be noted that for Ar and the other rare-gas atoms studied by us, there actually are found to be two points where $V_c^{\rm SR}$ and $V_c^{\rm LR}$ cross. For Ar, the crossings occur at 2.87 and 15.99 a_0. In all cases we have chosen the inner crossing for r_c in Eq. (13). It is our contention that polarization of the target atom becomes important well inside the outer crossing; the applications tend to bear this out. We know of no fundamental reason why the curves must cross, and there is no reason to choose the crossing as being particularly significant. We simply have found that the calculated phase shifts agree best with experiment and theory if V_c^{SR} and V_c^{LR} are joined near the inner crossing. The values of r_c (in a_0) obtained for the rare gases are 1.67 (He), 1.95 (Ne), 2.87 (Ar), 3.23 (Kr), and 3.67 (Xe); the respective polarizabilities used in these calculations[29] are 1.39, 2.66, 11.0, 16.7, and 27.2 a_0^3. It is interesting to note that the correlation potentials V_c^{SR} of the rare-gas atoms at the respective crossings are all within 10% of the argon value of -0.08 a.u. (The values for He, Ne, Kr, and Xe are -0.089, -0.092, -0.077, and -0.075, respectively.) If this observation is found to hold for a wider range of atoms and molecules, then one might suspect that the *ad hoc* prescription given here has some physical basis. We have examined the question for CO_2 by expanding V_c^{SR} in Legendre polynomials[4] and finding the crossings between the $\lambda=0$ and $\lambda=2$ contributions and the respective long-range forms $(\alpha_0/2)r^{-4}$ and $(\alpha_2/2)r^{-4}$, where α_0 and α_2 are the corresponding molecular polarizabilities. We find the crossings for $\lambda=0$ and 2 to occur at 3.14 and 3.20 a_0, respectively, where the respective contributions of V_c^{SR} have the values -0.09 and -0.04 a.u. (We understand from Norcross, who is studying the applicability of the present method to a series of molecules, that the trend observed here seems to hold for a wider variety of molecules, including polars.)

The full electron-atom potential energy, including the static potential $V_s(\vec{r})$ and the approximate exchange and correlation potentials described above, is

$$V(\vec{r})=V_s(\vec{r})+V_{\mathrm{FEG}}(\vec{r})+V_c(\vec{r})\ , \qquad (14)$$

where the static, exchange, and correlation contributions are shown for argon ($k=0.1$) in Fig. 1; Hara's modification[11] of the FEG exchange potential (HFEG) has been adopted for all calculations reported in this paper.

Finally, it must be emphasized that our use of electron-gas theory in the present model is not fully consistent in that the exchange potential V_{FEG} is taken to be energy dependent, while the correlation potential is not. In other words, in describing exchange we have taken great pains to avoid treating the projectile electron as an average electron in the Fermi sea; however, no such effort is made in our description of short-range correlation V_c^{SR}. While this inconsistency in the model is unsatisfactory, it may prove to be relatively unimportant. The most significant correlation effect at low energies is the long-range polarization interaction. In closer, where the local momentum can become quite large, the static and exchange potentials dominate. Thus the principal role of the short-range correlation potential V_c^{SR} in our model is to establish a cutoff radius for the polarization contribution. While the cutoff should in general depend on the energy, we expect the dependence to be weak for energies in the range treated here. The importance of including nonadiabatic corrections to the polarization potential for electron scattering has been discussed recently by Thirumalai and Truhlar,[30] who test various approximations applied to elastic electron-neon scattering.

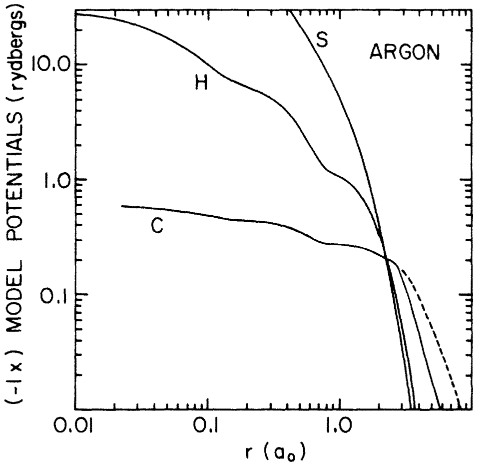

FIG. 1. Model electron-argon interaction potentials (multiplied by -1): static (S), HFEG exchange (H), correlation (C); – – –, FEG correlation outside the crossing.

III. APPLICATION TO ELASTIC SCATTERING FROM RARE-GAS ATOMS

We have chosen to illustrate the method by calculating phase shifts and cross sections for the elastic scattering of electrons by the rare-gas atoms He, Ne, Ar, Kr, and Xe since this sequence of closed-shell targets provides a range of electron densities and, therefore, should allow us to identify any density-dependent sources of systematic error in the approximation procedure being described and tested. For the spherically symmetric atomic targets, the radial partial-wave functions satisfy equations[1,2]

$$\left[\frac{d^2}{dr^2}+k^2-\frac{l(l+1)}{r^2}-2V(r)\right]u_{kl}(r)=0\ , \qquad (15)$$

where V is given by Eq. (14) and the "static" Coulomb potential is simply given by

$$V_s(r)=-\frac{2}{r}[Z-y_0(r)] \qquad (16)$$

in terms of the Coulomb repulsion term for an N-electron target atom

$$y_0(r)=\sum_{i=1}^{N}\left\{\int_0^r P_i^2(r')dr' + r\int_r^{\infty}[P_i^2(r')/r']dr'\right\}. \tag{17}$$

The bound atomic orbital functions $P_i(r)$ are taken to be the analytic Hartree-Fock functions of Clementi.[31] The radial electron density is given in terms of these orbitals by

$$\rho(r)=\frac{1}{4\pi r^2}\sum_{i=1}^{N}P_i^2(r)\ . \tag{18}$$

The radial equations (15) were solved using Numerov's algorithm with a modified Hermann-Skillman radial mesh (step size ranging from 0.001 25 to 0.04 a_0).[32] The asymptotic boundary conditions[1,2]

$$u_{kl}(r)\underset{r\to\infty}{\sim} a_{kl}[\hat{j}_l(kr)-\tan\eta_l\hat{n}_l(kr)]\ , \tag{19}$$

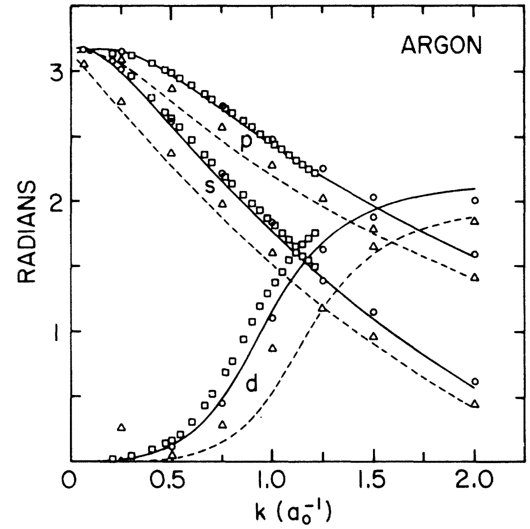

FIG. 2. Electron-argon elastic *s*, *p*, and *d* phase shifts: ——, model HC; — — —, model H (no correlation); Δ, static exchange (Ref. 39); ○, many-body perturbation theory (Ref. 39); □, experimental fits (Ref. 35).

TABLE I. Helium elastic electron-scattering phase shifts. Integral multiples of π have been removed.

k	H	HO	SE[a]	HC	HCO	EXPT.[b]	POL. ORB.[a]
				s wave			
0.0	(1.86)[c]	(1.63)	(1.48)	(1.37)	(1.26)		(1.11)
0.1	−0.186	−0.163	−0.148	−0.144	−0.134		−0.1213
0.2	−0.366	−0.323		−0.294	−0.275		
0.4	−0.694	−0.626	−0.574	−0.585	−0.555	−0.529	−0.5193
0.6	−0.970	−0.898	−0.830	−0.842	−0.810	−0.810	−0.7697
0.8	−1.193	−1.132	−1.056	−1.060	−1.032	−1.044	−0.9937
1.0	−1.374	−1.327	−1.252	−1.240	−1.218		−1.1886
2.0	1.236	1.243	1.279	1.347	1.351		1.3321
				p wave			
0.2	0.0013		0.003	0.0123			0.0128
0.4	0.013		0.024	0.0537		0.060	0.0594
0.6	0.037		0.067	0.120		0.127	0.1302
0.8	0.073		0.110	0.198		0.196	0.2081
1.0	0.116		0.183	0.269			0.2749
2.0	0.274		0.326	0.398			0.3941
				d wave			
0.4			0.0003	0.007		0.0056	0.0073
0.6	0.0013		0.0020	0.016		0.0132	0.0167
0.8	0.0045		0.0063	0.031		0.0251	0.0298
1.0	0.0104		0.0136	0.051			0.0458
2.0	0.0647		0.0735	0.156			0.1256

[a] Duxler, Poe, and LaBahn (Ref. 36).
[b] Williams (Ref. 35).
[c] Scattering length in a_0.

TABLE II. Neon elastic electron-scattering phase shifts. Integral multiples of π have been removed.

k	H	HO	SE[a]	HC	HCO	EXPT.[b]	SEPna[a]	POL ORB.[c]
				s wave				
0.0				(0.25)[d]	(0.24)		(0.347)	(0.172)
0.1	−0.120	−0.118		−0.050	−0.050		−0.0533	−0.040
0.2	−0.240	−0.237	−0.211	−0.133	−0.131		−0.132	−0.112
0.4	−0.478	−0.472	−0.426	−0.333	−0.330	−0.310	−0.328	−0.302
0.6	−0.708	−0.700		−0.551	−0.546	−0.523	−0.548	−0.516
0.8	−0.927	−0.918		−0.767	−0.762	−0.745	−0.771	−0.735
1.0	−1.133	−1.124	−1.064	−0.975	−0.970		−0.986	−0.946
2.0	1.195	1.199		1.314	1.316			1.326
				p wave				
0.1	−0.001	0.000		0.005	0.005		0.002	0.004
0.2	−0.018	−0.011		0.005	0.007	0.002	0.002	0.009
0.4	−0.105	−0.075		−0.031	−0.022	−0.019	−0.033	−0.008
0.6	−0.229	−0.185		−0.114	−0.098	−0.087	−0.111	−0.074
0.8	−0.356	−0.311	−0.269	−0.216	−0.199	−0.187	−0.210	−0.173
1.0	−0.472	−0.436	−0.391	−0.319	−0.306		−0.318	−0.285
2.0	−0.885	−0.882		−0.748	−0.747			−0.770
				d wave				
0.4	0.002			0.015		0.011		0.014
0.6	0.007			0.036		0.027		0.036
0.8	0.018			0.071		0.063		0.075
1.0	0.041		0.065	0.123			0.110	0.132
2.0	0.308			0.459				0.527

[a] Thirumalai and Truhlar (Ref. 30).

[b] Williams (Ref. 35).

[c] Thompson (Ref. 38).

[d] Scattering length in a_0.

where $\hat{j}_l(kr)$ and $\hat{n}_l(kr)$ are the Riccati-Bessel functions, η_l is the phase shift, and $k^2=2E$ is the incident electron's energy, were matched at $r=250\ a_0$, having determined that the results were unchanged by matching at larger distances.

The scattering orbitals $u_{kl}(r)$ that satisfy Eq. (15) are not guaranteed to be orthogonal to the bound orbitals $P_i(r)$ of like symmetry; however in most cases studied they are nearly so. We also carried out calculations in which this orthogonality was forced by the method of Lagrange multipliers in order to determine the importance of this additional constraint. The procedure[26,33] is to introduce Lagrange multipliers λ_α, thus expressing the scattering orbital for particular k,l as

$$u_{kl}(r)=u_{kl}^{0}(r)+\sum_{\alpha=1}^{\nu}\lambda_\alpha u_{kl}^{\alpha}(r)\ , \tag{20}$$

where $u_{kl}^{0}(r)$ is the solution to the homogeneous radial equation (15), and where each $u_{kl}^{\alpha}(r)$ is a solution to the inhomogeneous equation obtained by setting the right-hand side of Eq. (15) equal to one of the bound atomic radial orbitals $P_\alpha(r)$, where $\alpha=1,\ldots,\nu$ labels a particular orbital of given symmetry, e.g., $\alpha=1$ (1s), $\alpha=2$ (2s), etc. The values of the λ_α in Eq. (20) are obtained by solving the linear equations

$$\int_0^\infty u_{kl}(r)P_\alpha(r)dr=0,\quad \alpha=1,\ldots,\nu\ . \tag{21}$$

It actually makes sense to enforce this orthogonality only in the "static-exchange" approximation, i.e., when the correlation potential V_c is dropped in Eq. (14). However, since the most important contribution to the correlation potential is the long-range polarization energy, and since the orthogonality constraint changes the scattering orbitals only at relatively small distances, it is reasonable to assume that enforcing orthogonality with both exchange and correlation included will "improve" the treatment of exchange without contaminating the correlation. With the thought that these results might prove to be interesting we have calculated both exchange and

TABLE III. Argon elastic electron-scattering phase shifts. Integral multiples of π have been removed.

k	H	HO	SE[a]	HC	HCO	EXPT.[b]	POL. ORB.[a]	POL. ORB.[c]	MBPT[d]
					s wave				
0.0				(-1.37)[e]	(-1.35)		(-1.60)	(-1.416)	
0.089	-0.157	-0.155		0.0280	0.0288				
0.1	-0.175	-0.174	-0.151	0.0221	0.0230		0.049	0.034	
0.2	-0.351	-0.348	-0.304	-0.0805	-0.0790	-0.057	-0.039	-0.061	
0.4	-0.697	-0.692	-0.618	-0.395	-0.393	-0.346	-0.348	-0.374	
0.6	-1.030	-1.023	-0.940	-0.737	-0.735	-0.672	-0.696	-0.722	
0.8	-1.342	-1.336	-1.255	-1.069	-1.067	-1.011	-1.034	-1.063	
1.0	1.512	1.516	-1.552	-1.379	-1.378		-1.348	-1.382	-1.314
2.0	0.407	0.408	0.439[d]	0.563	0.564			0.548	0.613
					p wave				
0.1	-0.007	-0.004	-0.004	0.015	0.016		0.015	0.015	
0.2	-0.053	-0.039	-0.032	0.020	0.023	-0.006	0.026	0.027	
0.4	-0.253	-0.209	-0.178	-0.078	-0.067	-0.083	-0.055	-0.051	
0.6	-0.501	-0.449	-0.401	-0.273	-0.259	-0.252	-0.248	-0.245	
0.8	-0.739	-0.697	-0.643	-0.493	-0.481	-0.464	-0.473	-0.479	
1.0	-0.952	-0.926	-0.874	-0.706	-0.698		-0.694	-0.714	-0.670
2.0	1.401	1.402	1.406[d]	1.571	1.571			1.520	1.588
					d wave				
0.4	0.009		0.016	0.071		0.092	0.080	0.075	
0.6	0.055		0.102	0.228		0.303	0.312	0.274	
0.8	0.199		0.364	0.597		0.770	0.921	0.770	
1.0	0.533		0.854	1.157			1.546	1.360	1.098
2.0	1.872		1.837[d]	2.092				1.975	1.998

[a] Thompson (Ref. 37).

[b] Williams (Ref. 35).

[c] Thompson (Ref. 38).

[d] Pindzola and Kelly (Ref. 39).

[e] Scattering length in a_0.

exchange-correlation scattering results with and without the orthogonality constraint.

The calculated s-, p-, and d-wave phase shifts (HFEG and HFEG plus correlation, denoted H and HC, respectively) for Ar are compared in Fig. 2 with other theoretical static-exchange and correlation results and with fits to experimental data in order to illustrate the general nature of the results. Numerical values for scattering lengths and phase shifts for all the rare gases are given in Tables I—V in the approximations: H (HFEG), HO (orthogonalized HFEG), HC (HFEG plus correlation), and HCO (orthogonalized HFEG plus correlation). Also included in the tables for comparison are phase shifts from other sources, including EXPT. (experimental fits), SE (static exchange), POL. ORB. (polarized orbitals), MBPT (many-body perturbation theory), and SRPAE (random phase approximation). We have not compared our results with the approximate model-exchange polarized-orbital phase shifts of Yau *et al.*[34] since these are similar to the polarized-orbital results of Thompson.[38] We do include in Table II recent model-exchange nonadiabatic polarization results (SEPna) for neon.[30]

The argon phase shift comparisons in Fig. 2 and in Table III illustrate a number of features found to be common to the other rare gases as well. The HFEG approximation to exchange generally underestimates the strength of the (attractive) exchange potential, giving s, p, and d phase shifts that are smaller than "accurate" static-exchange results. (This has been noted by other authors.[23,25,26]) Imposing the orthogonality constraint increases the phase shifts. For s waves, these increases in phase shift at low energies are approximately given by $(0.2)k$ for He, $(0.02)k$ for Ne and Ar, and $(0.01)\,k$ for Kr and Xe, the coefficients of k in these expressions corresponding roughly to the accumulated inward shift of the nodes in the s-wave radial functions. The correction is large for He, a case where one

TABLE IV. Krypton elastic electron-scattering phase shifts. Integral multiples of π have been removed.

k	H	HO	HC	HCO
		s wave		
0.0			$(\cong -3.1)$[a]	$(\cong -3.1)$
0.1	−0.189	−0.188	0.0961	0.0969
0.2	−0.381	−0.380	−0.0156	−0.0147
0.4	−0.760	−0.758	−0.384	−0.383
0.6	−1.127	−1.124	−0.780	−0.779
0.8	−1.472	−1.470	−1.158	−1.157
1.0	1.350	1.352	−1.513	−1.512
2.0	0.115	0.115	0.284	0.285
		p wave		
0.1	−0.0092	−0.0055	0.023	0.024
0.2	−0.073	−0.053	0.029	0.034
0.4	−0.331	−0.277	−0.109	−0.096
0.6	−0.633	−0.577	−0.361	−0.348
0.8	−0.916	−0.876	−0.633	−0.624
1.0	−1.169	−1.145	−0.893	−0.887
2.0	1.017	1.018	1.197	1.197
		d wave		
0.1	0.0022	0.0020	0.0072	0.0072
0.2	0.0021	0.0021	0.0231	0.0231
0.4	0.0161	0.0161	0.116	0.116
0.6	0.0934	0.0935	0.382	0.382
0.8	0.3001	0.3002	0.8365	0.8365
1.0	0.6313	0.6317	1.1900	1.1901
2.0	1.1368	1.1372	1.3527	1.3528

[a] Scattering length in a_0.

might expect the electron-gas approximation to be particularly poor. The same reasoning applies to H_2, where a similar failing of the HFEG approximation has been noted by Morrison and Collins.[26] These authors showed that accurate phase shifts could be obtained for H_2 by adjusting the ionization potential I in Eq. (8), effectively making the exchange potential stronger and thereby shifting the node in the "s-wave" radial function inward. The influence of orthogonality on p-wave scattering is somewhat more striking, especially at low energies where the phase shifts are small due to the centrifugal barrier. For example, in Tables II–V, one sees that the orthogonality corrections to p-wave scattering at $k=0.4$ (2.18 eV) are 0.030 for Ne, 0.044 for Ar, 0.055 for Kr, and 0.059 for Xe. The correction is not even approximately linear in k since the positions of the nodes in the p-wave radial functions are sensitive to energy because of barrier penetration. The important observation, however, is that the orthogonality correction, while improving the phase shifts, does not give high accuracy. The SE comparisons in Fig. 2 and Table III for Ar adequately illustrate the situation for Ne, Kr, and Xe as well.

When correlation effects are included, via Eq. (13), the comparison of phase shifts with experiment[35] and with accurate polarized-orbital[36–38] or other methods that include correlation effects[39,40] is more encouraging, as illustrated in Fig. 2 for Ar. The situation is similar for the other rare gases (cf. Tables I–V). Total elastic scattering cross sections are illustrated in Figs. 3–7, where selected experimental results are given for comparison.[41–45] Agreement is good over a wide energy range, except at very low energies, where our combined HC exchange and polarization potentials are too weak to accurately reproduce the positions of the Ramsauer minima and the values of the scattering lengths. This is evident for Ar, illustrated in Fig. 2, where the HC s-wave phase shift is too small at small

TABLE V. Xenon elastic electron-scattering phase shifts. Integral multiples of π have been removed.

k	H	HO	SE[a]	HC	HCO	SRPAE[a]
s wave						
0.0				$(\cong -6)$[b]	$(\cong -6)$	
0.1	−0.260	−0.259	−0.227	0.125	0.127	−0.098
0.2	−0.479	−0.477		−0.019	−0.018	
0.4	−0.927	−0.925		−0.482	−0.480	
0.6	−1.357	−1.355		−0.962	−0.961	
0.8	1.381	1.382		−1.409	−1.408	
1.0	1.011	1.012	1.15	1.323	1.324	1.397
2.0	−0.405	−0.404		−0.214	−0.213	
p wave						
0.1	−0.041	−0.036		+0.009	+0.010	
0.2	−0.120	−0.095		0.030	0.034	
0.4	−0.449	−0.390		−0.158	−0.149	
0.6	−0.815	−0.762		−0.486	−0.477	
0.8	−1.155	−1.120		−0.825	−0.818	
1.0	−1.458	−1.439	−1.43	−1.145	−1.141	−1.18
2.0	0.521	0.522		0.719	0.719	
d wave						
0.2				0.024	0.024	
0.4	0.026	0.026		0.226	0.226	
0.6	0.191	0.191		0.797	0.798	
0.8	0.546	0.546		1.274	1.274	
1.0	0.859	0.859		1.387	1.387	
2.0	0.731	0.731		0.953	0.953	

[a] Amus'ya *et al.* (Ref. 40) (random phase approximation).

[b] Scattering length in a_0.

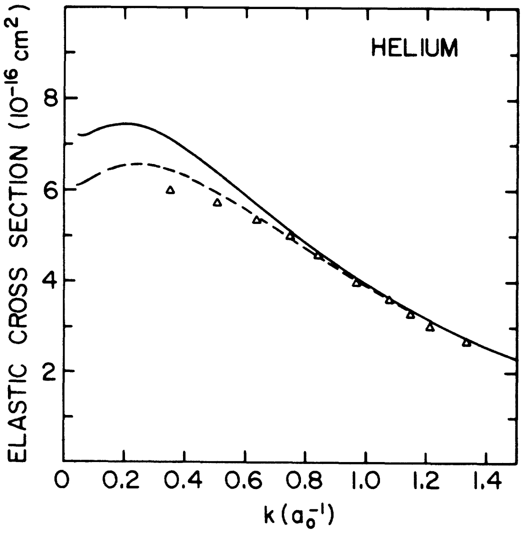

FIG. 3. Electron-helium elastic cross sections: ——, HC model; — — —, HCO model; Δ, experimental (Refs. 41, 42).

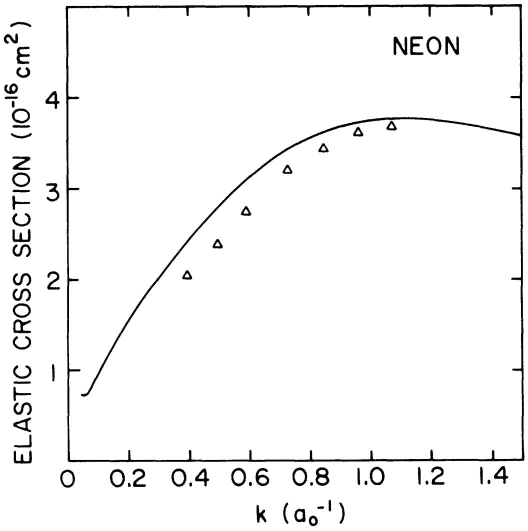

FIG. 4. Electron-neon elastic cross sections: ——, HC model; Δ, experimental (Ref. 41).

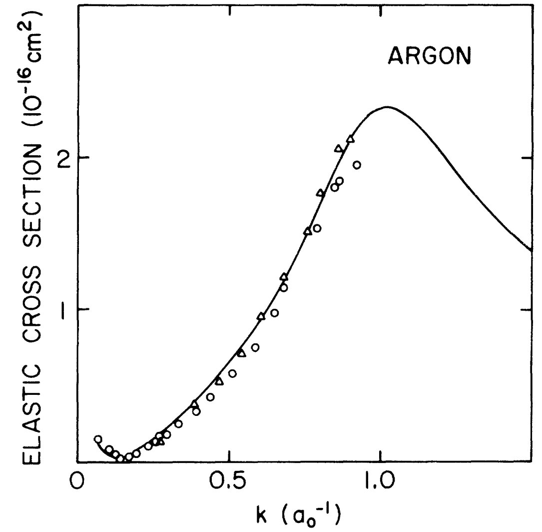

FIG. 5. Electron-argon elastic cross sections: ——, HC model; ○ and Δ, experimental (Refs. 43, 44).

values of k, by about $(0.15)k$, passing through 3π (note $\eta_0 - 2\pi$ is shown) at $k \simeq 0.13$ (0.23 eV); the observed Ramsauer minimum is located nearer to $k = 0.16$ (0.35 eV). The trend is evident in the cross sections illustrated in Figs. 3—7, where HCO results, shown for He, offer some improvement. For Ne-Xe, the HC and HCO cross sections are essentially identical. It should be noted that the HC result for the position of the "Ramsauer-minimum analog" in the p-wave phase shift[46] is much closer to the accurate value of $k = 0.30$. It is also notable that the HC scheme reproduces the d-wave resonance fairly well. Of course, for energies well below the centrifugal barrier, the $l \neq 0$ phase shifts are dominated by the long-range polarization interaction of Eq. (12), and errors in the short-range exchange and correlation interactions are of no consequence. The second peak located at about $k = 1.1$ in the electron-xenon cross section in Fig. 7 is due to an f-wave resonance.

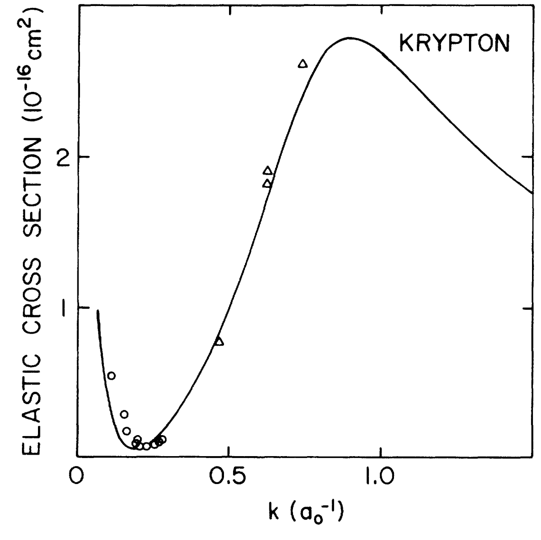

FIG. 6. Electron-krypton elastic cross sections: ——, HC model; ○ and Δ, experimental (Ref. 45).

IV. CONCLUSIONS

The method described here is a straightforward extension of the FEG exchange model to include correlation effects. In particular, it provides a continuous extrapolation of the long-range polarization potential to small distances. It is concluded from applications to elastic scattering of electrons by Ne, Ar, Kr, and Xe that the orthogonalization correction is unnecessary for s waves in that it removes only a small fraction of the error implicit in the HFEG exchange potential. For p waves, the effect of imposing orthogonality on the H or HC radial functions is more significant. For example, in the case of Ar, the HCO p-wave results in Table III are in better agreement with the most recent measurements and polarized-orbital calculations, except near the p-wave Ramsauer minimum, where uncertainty in both the theoretical and experimental phase shifts is likely to be larger. However, as pointed out earlier, the orthogonalization procedure applied to the HC model is questionable. In the case of He, the orthogonalization correction is larger and leads to improved agreement with polarized-orbital and experimental results. In summary, the comparisons described here suggest that the HC, and with caution the HCO, models of including exchange and

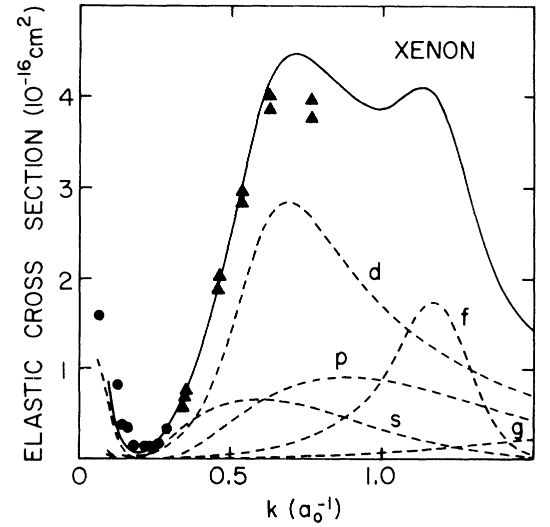

FIG. 7. Electron-xenon elastic cross sections: ——, HC model; — — —, HC model partial cross sections. ○ and Δ experimental (Ref. 45).

correlation in electron-scattering applications may provide an acceptable simple method for treating elastic electron scattering from complex molecules, clusters, or surfaces, where more rigorous approaches are too difficult.

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