SCREENING CORRECTION TO THE SLATER EXCHANGE POTENTIAL*

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A crystal potential which is local and eigenvalue-independent is of great practical advantage in calculations of energy bands in solids.[1] The exchange contribution to such a potential can be approximated by introducing a weighted average over occupied states.[2] For the free-electron gas, this average depends only on the density ρ; for a nonuniform system, one retains the free-electron form but stipulates that the density used be the local density $\rho(\vec{r})$ of the system in question. The potential is then given by the Slater formula[2]

$$V_{\text{ex}}(\vec{r}) = -6[(3/8\pi)\rho(\vec{r})]^{1/3}. \tag{1}$$

Energies are expressed in rydbergs and lengths in Bohr units throughout this Letter. Equation (1) has been employed extensively for the averaged exchange potential, both in atomic and in solid-state calculations. As pointed out by several authors,[1,3] it is much too large in the low-density tail of an atomic potential. This poses a particularly serious problem in computations on solids for which crystal potentials are constructed as sums of atomic potentials whose tails overlap. We have discovered that modifying the original Slater calculation to include the influence of electron correlation on pair interactions has the desired effect of decreasing the potential sharply in regions of low density. Moreover, at nearly <u>all</u> densities this correlation introduces a correction factor which is sufficiently severe to make itself felt in any calculation in which the choice of exchange potential is important. Olszewski[4] has given a formal treatment of the inclusion of correlation corrections such as we have in mind, but has not given a prescription for practical application. What we have done below consists, in effect, of replacing the Coulomb interaction e^2/r_{12} in the original Slater treatment of exchange by $(e^2/r_{12})\times\exp(-k_S r_{12})$, where k_S is an appropriate screening factor.

In the case of the uniform electron gas[5] the inclusion of correlation is essential and leads to a screened exchange interaction. We write the Fourier transform of the interaction as

$$\mathcal{V}(q) = V(q)/\epsilon(q), \tag{2}$$

where $V(q) = 4\pi e^2/q^2$ is the Fourier transform of the Coulomb interaction in cgs units and $\epsilon(q)$ is the dielectric function $\epsilon(q, q_0)$ for momentum transfer q in the limit of small q_0. The simplest screening which has the correct low- and high-q limits results from the linearized Thomas-Fermi (T-F) dielectric function,[5]

$$\epsilon(q) = 1 + k_S^{\,2} q^{-2}, \tag{3}$$

where $k_S = 0.82(r_S)^{1/2}k_F$, k_F is the Fermi momentum, and r_S is defined by $\rho^{-1} = (4\pi/3)r_S^{\,3}$. This dielectric function can be regarded as the small-q approximation to the random-phase approximation (RPA) result for the uniform electron gas.

With the interaction given by Eqs. (2) and (3), we can compute the averaged screened exchange potential as a function of the local density by essentially the Dirac procedure described in Appendix 22 of Slater's book.[2] The uniform-electron-gas average is

$$V_{\text{scr. ex.}} = -\frac{4}{\rho}\int\frac{d\vec{k}}{(2\pi)^3}\int\frac{d\vec{q}}{(2\pi)^3} f_{\vec{k}} f_{\vec{k}+\vec{q}}\,\mathcal{V}(q), \tag{4}$$

where $f_{\vec{k}}$ is the Fermi factor. Since $\mathcal{V}(q)$ is spherically symmetric, we integrate first over $\vec{k}$ and find

$$\begin{aligned} V_{\text{scr.ex.}} &= -\frac{k_F}{2\pi}\cdot\frac{4}{\pi}\int_0^1 dx\,(1 - \tfrac{3}{2}x + \tfrac{1}{2}x^3)(2k_F x)^2\,\mathcal{V}(2k_F x) \\ &= -6(k_F/2\pi)F(k_S/k_F) \\ &= -6[(3/8\pi)\rho(\vec{r})]^{1/3}F(k_S/k_F). \end{aligned} \tag{5}$$

$F(k_S/k_F)$ is a correction factor which depends only on the ratio $\alpha = k_s/k_F$. It is defined implicitly by Eq. (5), in which the remaining integration is easily performed when the T-F interaction is used:

$$F(\alpha) = 1 - \tfrac{4}{3}\alpha \tan^{-1}(2/\alpha) + \tfrac{1}{2}\alpha^2 \ln(1+4\alpha^{-2}) - \tfrac{1}{6}\alpha^2[1 - \tfrac{1}{4}\alpha^2 \ln(1+4\alpha^{-2})]. \tag{6}$$

We note that for $k_s = 0$, which corresponds to no screening, F is unity and Eq. (5) reduces to the Slater potential. In the limit of complete screening ($k_s = \infty$), F vanishes. Since

$$\alpha = k_s/k_F = 0.82(3/4\pi\rho)^{1/6} = 0.646\,\rho^{-1/6}, \tag{7}$$

the reduction of the Slater potential by the correlation factor F is density-dependent and becomes more severe as the density decreases, as shown in Fig. 1. As pointed out by Slater, the simple model of a Fermi hole containing total charge $+e$ distributed uniformly gives a qualitatively correct description of the average exchange potential. The same is true for the average screened exchange (5) and (6) provided one remembers to use the screened interaction in computing the potential at the center of the hole.

The quantitative effect of the correlation factor can be quite pronounced in practical cases. As an example we consider the exchange contribution to the crystal potential in a chloride such as AgCl, where the crystal potential might be constructed as a sum of ionic potentials on the lattice sites. In Fig. 2 we plot r times the averaged exchange potential both with and without screening for Cl$^-$ as a function of distance. The densities employed were obtained from numerical Hartree-Fock calculations on the free ions.[6] As suggested by Fig. 2, the contribution of a Slater exchange potential to the electronic energies in a tight-binding calculation of the valence band is enormous; in fact, in AgCl it is about twice that of the Madelung energy, a clearly unacceptable situation. The Thomas-Fermi screening reduces the exchange contribution by a factor of about 10. A similar situation will obtain in all ionic crystals. It is likely, for example, that Casella's computed lower limit[7] to the width of the $3p$ band of NaCl will be reduced. Since the correlation correction is felt at nearly all distances from the nucleus, the contribution of exchange to long-wavelength Fourier components of the potential will be affected in many OPW calculations. This will be particularly important in the computation of the $\vec{K} = 0$ Fourier coefficient of the potential for which it is well known that the original Slater formula gives too large a value[1,8]; the use of screened Slater exchange may remove the need for the introduction of arbitrary cutoffs

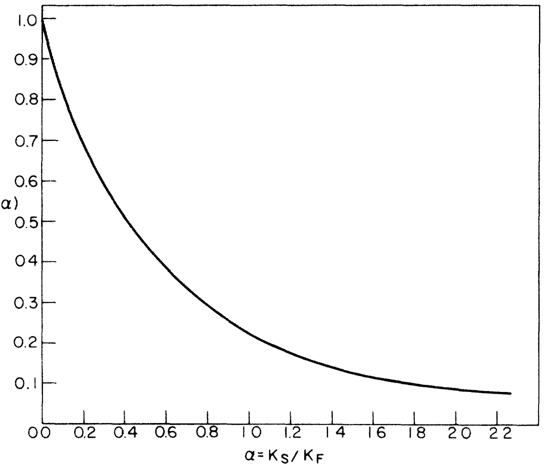

FIG. 1. Correction factor, due to correlation effects, which is to multiply the Slater averaged exchange potential. The abscissa is $\alpha = 0.646\,\rho^{-1/6}$, where k_s and k_F are the screening factor and Fermi momentum, respectively.

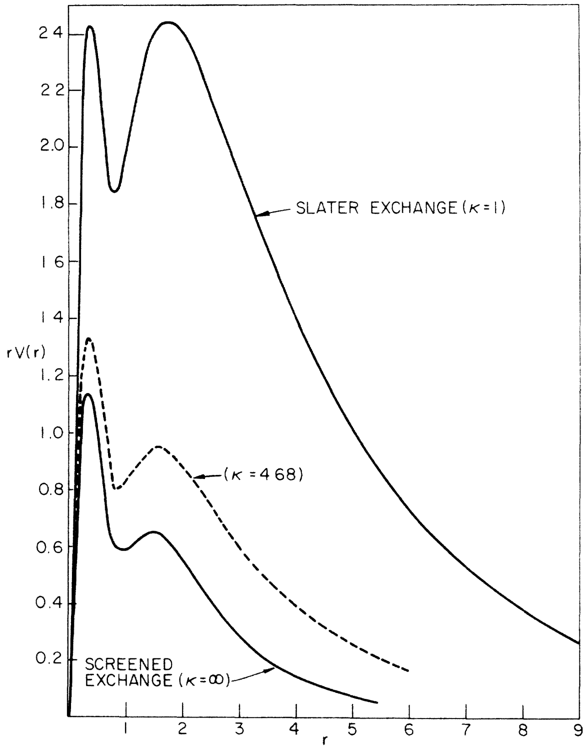

FIG. 2. Comparison of effective exchange potentials V for Cl$^-$. The ordinate is rV in units of ry $\times a_0$, and the abscissa represents the distance r from the nucleus in units of the Bohr radius, a_0. The parameter κ is defined in connection with Eq. (9).

in the potential. We have also applied the correction factor to the traditional test case Cu^+, which was studied by Pratt[9] and by Hartree.[10] The new potential is closer than the old to the Hartree-Fock self-consistent potential seen by a $3d$ electron. While this fact has no particular quantitative significance, it suggests that the screened potential, applied in atomic calculations, will not give results vastly different from "self-consistent" calculations.

We have considered in some detail the justification, within the context of the RPA, of the use of the Thomas-Fermi dielectric function. Neglecting the plasmon contribution, we find that for densities of interest here the total interaction energy computed exactly within the RPA agrees, to within 1%, with that obtained using the simpler Thomas-Fermi screening.

We have also considered the possibility that our correction overestimates the effect of correlation, since the T-F screening is too strong for low densities at small q. We might modify Eq. (3) in such a way that $\epsilon(q)$ reduces to some empirical dielectric constant κ at $q \to 0$:

$$\epsilon(q) = 1 + k_s^2/(q^2 + q_s^2), \tag{9}$$

with $q_s^2 = k_s^2/(\kappa - 1)$. It is found that in practice any $\kappa \geq 4$ yields an effective exchange potential much closer to the screened potential ($\kappa \to \infty$) than to the unscreened potential ($\kappa = 1$); this is illustrated in Fig. 2.

We emphasize that our procedure, like that of Slater, is based on a uniform-electron-gas approximation for local regions. Although its validity in regions of rapidly varying density is limited,[10,11] it is likely to be less susceptible to criticism on these grounds because the particle-particle interactions involved are screened. We conjecture, then, that our approximate potential is never poorer than the original Slater potential; it has a much shorter range and incorporates a correction which is known to be important in the uniform electron gas.

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LOW-MASS ANOMALY IN PHOTOPRODUCTION OF PION PAIRS

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Abashian, Booth, and Crowe[1] have observed an anomaly in the production of pion pairs in the reaction

$$p + d \to He^3 + 2\pi.$$

This anomaly (referred to hereafter as "ABC") occurs in the isotopic spin state $T = 0$ of the two pions and may be interpreted as being caused by a final-state interaction of the two pions or as being caused by the production of some particle. The most popular explanation of the ABC at the present time is that it is caused by a strong S-wave π-π interaction which can be characterized by a scattering length.[1-3] For convenience, the ABC will be referred to in the following as if it were a particle.

Several previous experiments[4-6] have attempted to observe the ABC in photoproduction from hydrogen. Bernardini et al.[4] used photons of about 750 MeV, and detecting only the recoil proton, observed no effect. They gave an upper limit to the cross section of 0.3×10^{-30} cm^2/sr. Gomez