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PHYSICAL REVIEW A VOLUME 7, NUMBER 4 APRIL 1973

Low-Energy-Electron Scattering Amplitudes. II. Validity of Free-Electron-Gas Exchange Approximations Applied to Electrons Incident on Hg

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(Received 6 July 1971)

For the test case of 300-eV electrons incident on Hg the influence of the exchange of the incoming electron with the atomic electrons is studied. Four different approximations for the derivation of an exchange potential based on the free-electron-gas description are discussed. These approximate exchange potentials were employed in calculations of electron scattering factors. The comparison of those results with a rigorous Hartree–Fock (HF) treatment of the total scattering problem ($N+1$ particles) shows that the exchange given by Kohn and Sham is too large, especially at large atomic distances. By Gombás's introduction of a cutoff at the radius of the Thomas–Fermi–Dirac atom, the long tail of the potential was avoided. While the truncated results of Gombás decrease the deviations significantly, a different treatment of the self-exchange as suggested by Lindgren and Rosen brings the best agreement with the HF calculation. The theoretical results show that precise relative measurements in the valleys of the different cross sections are an extremely sensitive tool for testing scattering theory.

I. INTRODUCTION

At present there are two rather different approaches employed in calculating elastic differential cross sections for moderate-energy electrons (300 eV) incident on gaseous systems. The extended polarization potential approximation of LaBahn and Callaway treats the scattering problem by Hartree–Fock (HF) perturbation theory.[1] This approach takes into account adiabatic (energy-independent) charge cloud polarization effects and exchange of atomic electrons with each other as well as with the incoming electrons. However, correlation effects have to be neglected, and the method is too complicated to be extended to heavy atoms like Hg.

The second technique used to calculate scattered intensities is based on the static-potential theory. This approach utilizes the best available wave functions of the unperturbed target to calculate cross sections, spin polarization, and other effects.[2] It can be applied to any atom. However, the changes of the differential cross sections due to such effects as the exchange of the incoming electrons and the charge cloud polarization have to be calculated by finding correction terms to the static atomic potential. With this corrected potential, new scattering factors are calculated which include the effects in an approximate way. It is our purpose to compare the various approximate corrections to the static potential that have been proposed to account for exchange scattering. We will then discuss the effects of these exchange potentials on the corresponding theoretical elastic differential cross sections.

The exchange of all electrons can be included rigorously for electrons scattered from an N-electron atom by numerically solving the $N+1$ many-body problem with a HF treatment, as was done by Walker for Hg.[3] With respect to the effect of exchange between the incoming electron and the atomic electrons, these cross sections are considered to be the "exact solution" to the scattering problem. However, there can still be considerable disagreement between Walker's results and the experimental data since charge cloud polarization effects are not yet included in his approach. These "exact solutions" offer the possibility of studying by comparison the various exchange calculations based on the free-electron-gas exchange approximations. The degree of agreement between the $(N+1)$-electron solutions and those employing various exchange approximations is very interesting for two reasons. First, exchange potentials are of considerable interest to solid-state calculations, since normally only analytic potentials are employed in calculations for solid materials (see, for instance, the pseudopotential treatment by Phillips and Kleinman[4]). Second, Walker's approach has given scattering factors which include the total exchange rigorously, but the method is very involved and requires extensive computer efforts.

In the next section the exchange potentials employed in our calculations, based on the free-electron-gas model, will be discussed. Their influence on the scattering amplitudes will be presented and compared with Walker's results in Sec. III. In Sec. IV some final conclusions will be drawn.

II. EXCHANGE POTENTIALS

The most detailed discussion of the various proposed exchange potentials based on the free-electron-gas assumption was given by Wilson *et al.*[5] All the exchange potentials they discussed have basically the same analytic form:

$$V_{\mathrm{ex}} = 4F(\eta)\,[(3/\pi)\rho]^{1/3}\,, \tag{1}$$

where $F(\eta)$ is a function characterizing the different approximations, η is the ratio of the momentum k of an incoming electron to the momentum k_F of an electron at the Fermi level of the target atom, and ρ is the electron density distribution of the target atom. For an electron gas that obeys Fermi statistics, $F(\eta)$ is given by

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

If one assumes, as did Kohn and Sham,[6] that only those electrons located at the Fermi level contribute to the exchange in the scattering process, then $\eta = 1$ and $F(\eta) = \frac{1}{2}$.

Another useful approximation to $F(\eta)$ was first proposed by Gombás.[7] He introduced an additional constraint on the exchange potential by arguing that the statistical approach has to break down in regions where the electron density is low. Therefore the exchange potential in the Gombás approximation is forced to zero at the boundary of the Thomas–Fermi–Dirac (TFD) atom. To enforce this boundary condition Gombás introduced a correction function S such that the exchange potential is given by

$$V_{\mathrm{ex}} = 4F(\eta)\,[(3/\pi)\rho]^{1/3}\,[1 - S(\eta_0)], \tag{3}$$

where

$$S(\eta_0) = \eta_0 - \tfrac{1}{2}(1-\eta_0^2)\ln\left|\frac{1+\eta_0}{1-\eta_0}\right| \tag{4}$$

and η_0 is given by

$$\eta_0 = k_0/k_F = (\rho_0/\rho)^{1/3}\,,$$

k_0 and ρ_0 being, respectively, the magnitude of the momentum and the electron density at the boundary of the TFD atom. Gombás applied his approximation to different atoms and ions and found that only the first term in Eq. (4) is important. The value of ρ_0 was given by Gombás as

$$\rho_0 = 0.002127(1/a_0^3)\,.$$

In the free-electron-gas approximation to the exchange process, a significant improvement may be made in the accuracy of $F(\eta)$ as stated in Eq. (2). The derivation of $F(\eta)$ accounts for the fact that an electron cannot exchange with itself and, therefore, creates a Fermi hole in phase space. However, integration over the exchange interactions is carried out over the total phase space, thereby including the Fermi hole. Thus, due to the integration limits, part of the self-interaction is brought back into the exchange. (The HF method avoids this problem because the self-exchange term exactly cancels with the self-Coulomb contribution.) Lindgren and Rosén[8] showed that the problem of self-exchange can be avoided by introducing the corrected exchange potential

$$V_{\mathrm{ex}} = 4F(\eta)\,[(3/\pi)\rho]^{1/3}\,[1 - (2/z)^{1/3}]\,, \tag{6}$$

where z is the atomic number of the target atom. Gombás[9] has also derived an exchange potential corrected for self-exchange, but this correction results in the somewhat different expression

$$V_{\mathrm{ex}} = 4F(\eta)\,[(3/\pi)\rho]^{1/3}\,(1 - 2/z)^{1/3}. \tag{7}$$

Altogether, four different exchange approximations have been considered, each leading to a scattering potential which may be used to calculate the corresponding differential cross section: first, Kohn and Sham's $\eta = 1$ approximation; second, Gombás's cutoff of the exchange tail at ρ_0; third, Lindgren and Rosén's result correcting for self-exchange and including Gombás's exchange tail cutoff; and fourth, Gombás's expression including both a self-exchange correction and a cutoff in the exchange tail.

III. THEORETICAL ELASTIC DIFFERENTIAL CROSS SECTIONS

Differential elastic cross sections have been calculated employing a program which computes from a static atomic potential the phase shifts η_l and η_{-l-1} as well as the relativistic scattering amplitudes f and g.[10] The atomic potential was a relativistic Hartree potential, employing the free-electron-gas exchange approximation to correct for the exchange of the atomic electrons (HFS).[11] The fact that all of the exchange potentials considered here lead to differential cross sections which agree with experimental data within the experimental uncertainties (especially at large angles) implies that a meaningful comparison between theoretical cross sections must be based on a study of the numerical results. Walker's rigorous HF calculations were considered the standard for comparison with the other theoretical calculations. Walker[3] provided partial-wave phase shifts only up to $l = 10$. This was justified by the fact that exchange effects are visible only up to $l = 7$, although the phase shifts have not decreased enough to be negligible. Therefore, all theoretical calculations were performed using only ten partial waves, which allows direct comparison with Walker's results, but prevents comparison of these results with experimental data.

A set of partial waves calculated using a relativistic HF potential (HFD) successfully reproduced Walker's HF N-particle results (neglecting exchange of the incoming electron) to all significant figures. The phase shifts calculated using the HFS potential also agreed very well with Walker's phase shifts, the deviations from Walker's results being about one order of magnitude smaller than those caused by the introduction of an exchange term in subsequent calculations. However, the deviations between the HFD and HFS calculations indicate the extreme sensitivity of electron scattering to very small variations in the scattering potential.

The exchange potentials proposed by Gombás and by Lindgren and Rosén are reproduced by Fig. 1. The cutoff points and the corrections for self-exchange are obvious in the figure. The percentage presentation shows that the exchange potentials greatly affect the total scattering potential, but only to a very definite radial distance from the nucleus. It should be noted that very little change is found in the theoretical forward scattering amplitudes due to exchange effects. This agrees with the prediction of the first Born approximation that the contribution of the exchange effect to the scattered intensity vanishes like S^2 when S approaches zero $[S = (4\pi/\lambda)\sin\frac{1}{2}\theta]$.

Figures 2 and 3 show the scattering factors calculated from a HFD potential combined with each of the four previously discussed exchange potentials. Also shown in these figures is the "exact" result calculated from Walker's partial-wave phase shifts. Since the exchange effects account for only about 10% of the total of each scattering factor, the figures drawn are actually the differences between the HFS calculation and the calculations based on the exchange potentials. The HFS calculation was chosen as the basis for comparison because of its easy availability to anyone wishing to compare their results with those presented here. It can be seen in Fig. 2 that all additions to the atomic potential used to account for exchange create in f the amplitude oscillations caused by the Legendre polynomials in the partial-wave ex-

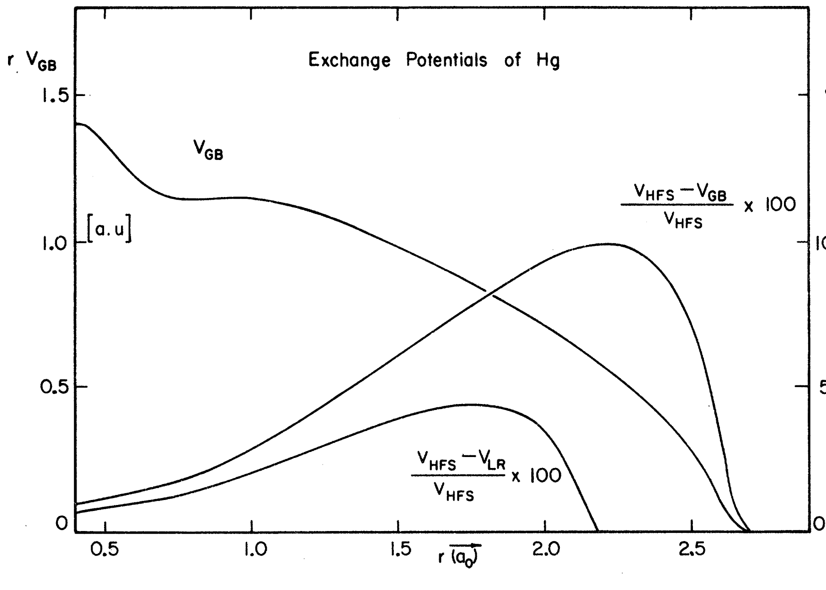

FIG. 1. Exchange potential V_{GB} for Hg proposed by Gombás [Eq. (3)] (for convenience rV_{GB} is plotted). The percentage additions to the atomic HFS potentials are also given for V_{GB} and V_{LR}, where V_{LR} is calculated according to Eq. (6).

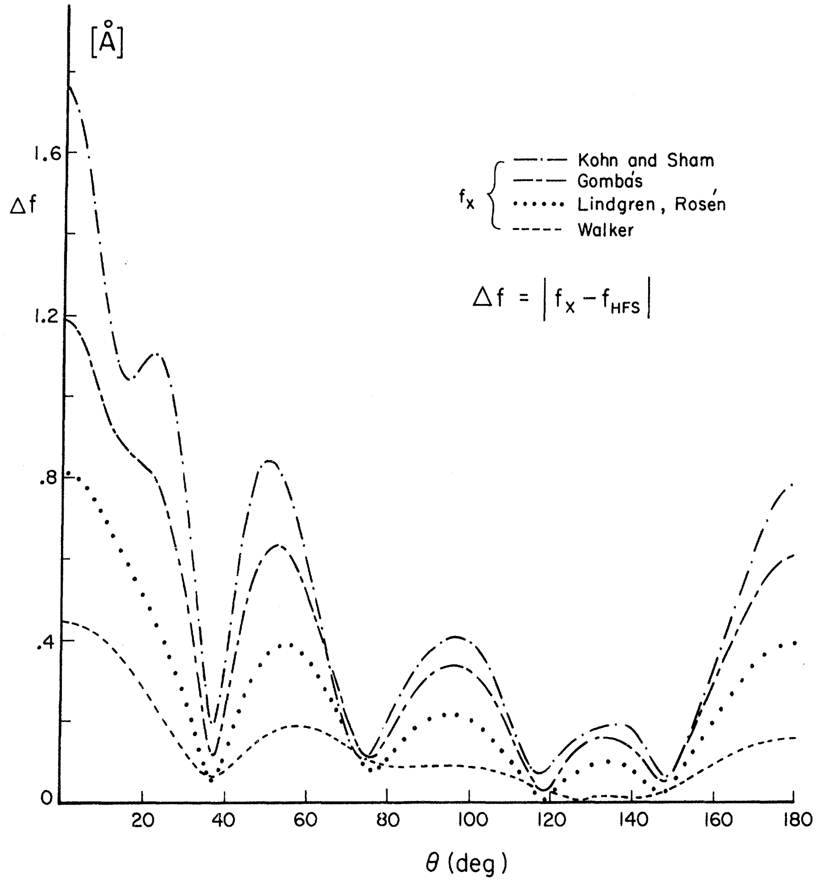

FIG. 2. Changes in the scattering amplitudes *f* for 300-eV electrons incident on Hg due to the various exchange potentials. Walker's rigorous HF results give the difference curve which is considered exact.

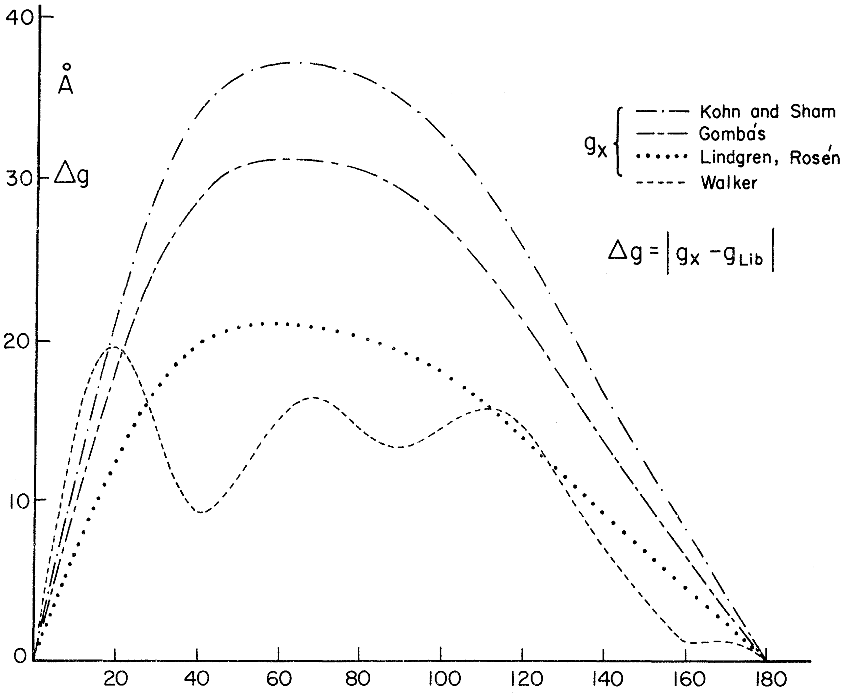

FIG. 3. Differences in the electron scattering amplitudes *g* describing the contributions of the spin-flip process to the cross section for 300-eV electrons incident on Hg. The "exact" results of Walker show oscillations, which are introduced by the trunction of the partial-wave phase shifts given in Ref. 3.

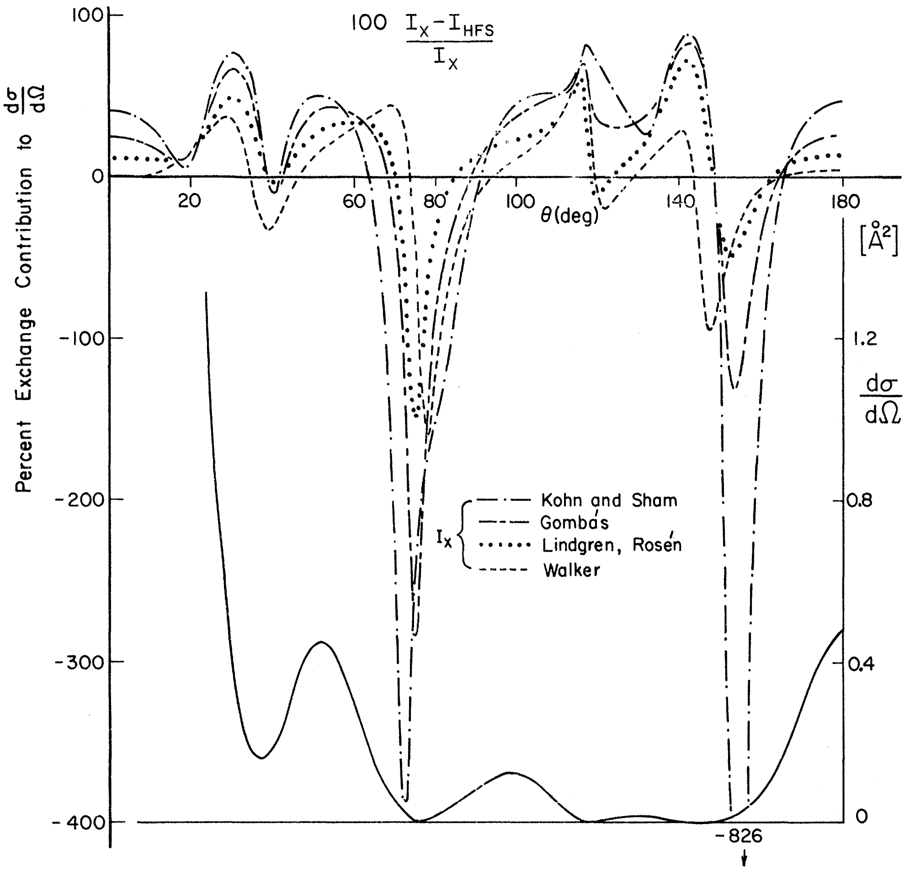

FIG. 4. Percentage changes of the differential cross section of 300-eV electrons scattered elastically from Hg owing to incorporation of the exchange potentials. The differential cross section is shown for comparison.

pansion. Furthermore, it is evident in Fig. 2 that Kohn and Sham's exchange approximation strongly over-emphasizes the effects of exchange and causes a significant increase in the forward scattering due to the long range of $\rho^{1/3}$.

The cutoff of the exchange potential tail introduced by Gombás [Eq. (3)] reduces the forward scattering, and, indeed, improves the agreement with the "ideal" calculation at all angles. The agreement is improved further by the correction for self-exchange proposed by Lindgren and Rosén [Eq. (6)].

The same type of behavior is observed if one examines the effect of the exchange on the *g* amplitude. In Fig. 3, we see again that Kohn and Sham's approximation overestimates the influence of exchange, and again the additional corrections bring the *g* values much closer to Walker's "ideal" result. The oscillations in Walker's *g* amplitudes are very likely produced by the rounding errors of the partial-wave phase shifts. (Walker's phase shifts are given to only three digits.) It was found that the introduction of Gombás's[12] self-exchange correction [Eq. (7)], when compared to Gombás's previous approximation [Eq. (3)], affected the results by less than 1% at all scattering angles. Unfortunately, there is no experiment known at this time which measures the exchange contribution directly. It is obvious that when comparing calculations resulting from different approximations, percentage differences in the differential cross sections are greatest at angles where the scattered intensity is at a minimum. Therefore, Fig. 4 gives the deviations in percent of the scattered intensities, calculated from the various exchange approximations, compared to the HFS calculation. This shows how precise and at which angles a scattering experiment must be performed to detect these deviations.

Figure 5 shows the results of a set of calculations intended to study the sensitivity of the previous results to the choice of the cutoff density ρ_0. When ρ_0 was changed from the value given in Eq. (5) to

$$\tilde{\rho}_0 = 0.003074(1/a_0^3) , \qquad (8)$$

where $\tilde{\rho}_0$ determines the cutoff density of a correlated TFD atom, it was found that the scattering factors changed very little from those calculated using ρ_0. This shows that the specific choice of a cutoff density is not very critical.

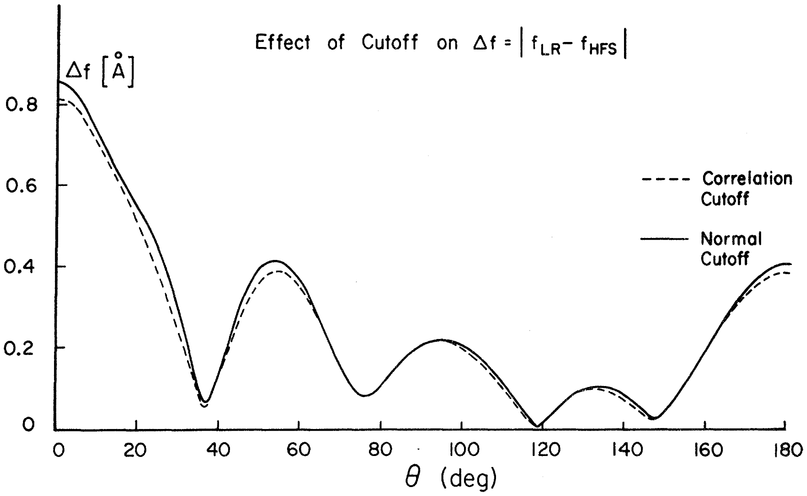

FIG. 5. Changes in the scattering amplitudes due to variations in the cutoff parameter. The normal cutoff is given by Eq. (5), the correlated one by Eq. (8). The exchange approximation proposed by Lindgren and Rosén was used in the calculation of f_{LR}.

IV. DISCUSSION AND CONCLUSIONS

In the previous section it was shown that the exchange of the incoming electron with the atomic electrons influences the differential cross section remarkably at selected scattering angles. From the various graphs showing the scattering quantities it can be concluded that the free-electron-gas exchange potential in the truncated form, and with the proper correction term for self-exchange, is a fairly accurate approximation to the actual exchange potential.

From Fig. 4 it is obvious that the exchange contribution to $I(\theta = 0°)$ is small. Furthermore, one can conclude that only precise experimental data in the valleys of the differential cross section can tell us more about the agreement between theory and experiment. In addition, it can be seen that relative measurements of the differential cross section are sufficient if a maximum (for matching) is included in the experimentally covered angular range.

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*Research supported by the Joint Services Electronic Program under Research Contract No. F44620-71-C-0091.

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