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Experimental Determination of the Correlation Effects in the Total Differential Electron Cross Section. I. Ne†‡

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The relative total differential electron cross section (elastic plus inelastic scattering) for Ne was measured with an accuracy of 0.25%. The experimental data were compared with scattering factors calculated with the first Born approximation using a Hartree-Fock wave function and a configuration-interaction wave function giving 86% of the atomic electronic correlation energy. The comparison is in very good agreement with the recently published first-Born-approximation scattering factors employing this configuration-interaction wave function. The measurements prove that electron diffraction can be a useful experimental tool for studying correlation effects on the scattered intensity with an accuracy of at least 20% in atoms and molecules.

I. INTRODUCTION

Recently, Tavard and co-workers have shown that electron diffraction data are directly connected in the first Born approximation to the total energy of a target atom or molecule. [1–3] This knowledge together with the relation between the elastic differential cross section and the first-order density matrix of the scatterer, and between the total inelastic differential cross section and the second-order density matrix, makes electron diffraction an attractive experimental tool for testing wave functions.

In order to apply these relationships, experiments have to be made so that a number of conditions are fulfilled. For instance, the first nonrelativistic Born approximation must be valid, scattering must take place from isolated atoms and no multiple scattering effects must take place involving different target atoms. Conventional electron diffraction equipment [4–6] is able to meet these conditions by scattering keV electrons (i.e., in the range $\sim 40 \pm 20$ keV) from atoms or molecules as long as the atomic numbers are small.

In Sec. II, a short review of the present state of knowledge on scattering theory and atomic many-body theory is given as far as it is of concern to the present experiments. In Sec. III, a description of the scattering apparatus is given, and in Sec. IV, the results of the comparison between theory and experiment, together with the experimental uncertainties, are presented.

II. THEORY

Within the framework of the first Born approximation, [7] the total (= elastic + inelastic) differential cross section for electrons scattered from atoms is given by[8]

$$I_{\text{total}} = \frac{I_0}{s^4} \langle \psi | | Z - \sum_{\mu=1}^{N} e^{i\vec{s}\cdot\vec{r}_\mu} |^2 | \psi \rangle , \qquad (1)$$

where I_0 is a constant proportional to the product of the electron beam current and the density of the gas beam, $\hbar s$ is the magnitude of the momentum transfer during the collision, Z is the atomic number, N is the number of electrons in the scatterer, and r_μ is the distance from the c.m. to the μth atomic electron. Note that the c.m. and the position of the nucleus can be assumed to be equivalent under the experimental conditions considered here. Introducing into Eq. (1) the diagonal part of the first-order density matrix or the electron density function

$$\rho(r) = \langle \psi | \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_1) | \psi \rangle , \qquad (2)$$

and the electron-pair probability density

$$\rho_c(\vec{r}) = \langle \psi | \sum_{i \neq \nu}^{N} \sum^{N} \delta(\vec{r} - \vec{r}_i + \vec{r}_\nu) | \psi \rangle , \qquad (3)$$

the total differential cross section can be written

$$I_{\text{total}} = \frac{I_0}{s^4} \left[Z^2 + Z + \int d\vec{r} \rho_c(\vec{r}) e^{i\vec{s}\cdot\vec{r}} - 2Z \int d\vec{r} \rho(\vec{r}) e^{i\vec{s}\cdot\vec{r}} \right] . \qquad (4)$$

Equation (4) is the scattered intensity assuming the incident electrons approach the atom from a fixed direction. In order to get the measured

total scattered intensity, Eq. (4) has to be averaged over all possible orientations of the atomic coordinate system with the result

$$I_{\text{total}} = \frac{1}{4\pi}\int I_{\text{total}}(\vec{s})\,d\Omega_s = \frac{I_0}{s^4} \times \left[Z^2 + Z + \int_0^\infty dr j_0(sr) \int d\Omega\, r^2 \rho_c(\vec{r}) - 2Z \int_0^\infty dr j_0(sr) \int d\Omega\, r^2 \rho(\vec{r}) \right] . \quad (5)$$

Introducing the commonly used $D(r)$ and $P(r)$ functions, which represent the electron radial distribution function and the electron-pair correlation function defined as

$$D(r) = r^2 \int d\Omega \rho(\vec{r}) ,$$

$$P(r) = r^2 \int d\Omega \rho_c(\vec{r}) ,$$

I_{total} can be written

$$I_{\text{total}} = \frac{I_0}{s^4} \left[Z^2 + Z + \int_0^\infty dr j_0(sr) P(r) - 2Z \int_0^\infty dr j_0(sr) D(r) \right] . \quad (6)$$

Equation (6) shows the direct connection between electron scattering and the first- and second-order density matrices.[8] Since $\rho(\vec{r})$ with $\rho_c(\vec{r})$ are quantities obtainable from wave functions, electron scattering should provide an excellent tool for comparing the detailed nature of charge densities obtained from wave functions with experimental data to the extent that the first Born theory is valid. Analogous equations have been derived for the case where a molecule is the scattering target.[1-3,8] Since Eq. (6) has to be fulfilled for each scattering angle, the theory predicts a function of a single variable (differential cross section) which has to agree with recorded data, point by point. Usually theory and experiment are compared in terms of properties expressed only as single numbers such as magnetic susceptibilities or nuclear shielding constants. The total scattered intensity I_{total} can be divided into elastic and inelastic parts. These can be written in terms of the $D(r)$ and $P(r)$ functions as (we are still within the framework of the first Born approximation)

$$I_{\text{el}} = \text{const} \times s^4 (Z - F_x)^2 \quad (7)$$

and

$$I_{\text{inel}} = \text{const} \times s^4 [Z - F_x^{\,2} + \int_0^\infty dr P(r) j_0(sr)], \quad (8)$$

where $F_x = \int_0^\infty dr D(r) j_0(sr)$.

Equations (7) and (8) show that the elastic scattering depends only on the one-electron density of the atom, whereas, the inelastic scattering depends on the electron-pair correlation function, $P(r)$, which is more sensitive to correlation effects. The elastic and inelastic scattered intensities have been calculated using a configuration-interaction (CI) wave function giving 86% of the atomic electronic correlation energy for Ne. The authors calculated elastically scattered intensities by using both the first Born approximation and the partial-wave method.[9] The former are compared in Fig. 1 with the values published by Tavard and co-workers[10] calculated with Eqs. (7) and (8) with a Hartree-Fock (HF) wave function. The differences between HF and CI results are somewhat small but still make some contributions to the deviations in the total intensity from correlation effects. The inelastic scattering is more sensitive to the choice of the wave function and suggests that scattering experiments may offer a means of[11] studying the nature of the electron-pair correlation function. As far as we know, scattering experiments offer the only currently available experimental approach for making such studies. Note that the deviations in the inelastic scattering are large enough that they cause appreciable changes in the total differential cross sec-

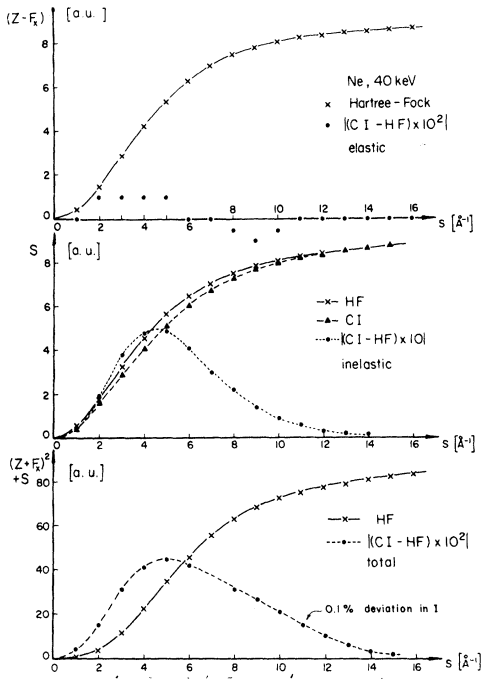

FIG. 1. Calculated electron scattering factors for Ne as a function of $s = (4\pi/\lambda)\sin\frac{1}{2}\theta$.

tion. From Fig. 1, it can be seen that a measurement executed with Ne with an accuracy of 0.25% would be able to test the validity of the first Born approximation and possibly allow for the study of correlation effects in atoms. When molecules are chosen as a target gas, completely analogous arguments are valid.[12] In addition, in the molecular case it is possible to get information on the molecular binding energy as well as charge densities. At present, computational techniques do not easily allow the calculation of correlated wave functions for molecules due to the complexity of the many-body problem. Therefore, the current electron scattering experiments could serve as an aid in solving problems in quantum chemistry.[8,11,13-15]

III. EXPERIMENTAL PROCEDURE

Since the experimental technology will be described elsewhere,[16] only a short description of the apparatus will be given here. In general, an electron scattering apparatus consists of three parts; an electron beam, an atomic or molecule gas jet, and a detector device. In Fig. 2, a sketch of the experiment is presented.

The electron beam was produced by a telefocus-electron gun and an accelerating voltage of 40 kV was employed with the wavelength measured to 0.01% by means of a divider resistor, a typical beam current was 20 μA. The primary beam was trapped by a Faraday cage after the electrons were bent electrostatically by 90°. This technique decreased the intensity of background scattered electrons considerably. Fluctuations in the intensity of the electron beam were eliminated by integrating the charge of the electron beam over the time period of each measured point and then reducing all recorded data to charge unity.

The Ne-atom beam was formed by expanding the gas through a nozzle of 0.5 mm in diam. and 4-mm throat length into the vacuum. The vacuum was 2×10^{-6} Torr without a gas beam and 1×10^{-5} Torr when Ne gas was injected. Gas flow rates were on the order of 10^{19} molecules/sec. After the electron beam and the gas beam were adjusted so that they crossed each other the angular distribution of the scattered electrons was measured with a scintillator mounted on a photomultiplier fastened to a scanning arm which turned on a circle with its center in the scattering volume. The scattering angle zero was determined by measuring the scattering distribution over a 10° range on both the right-hand side and left-hand side of the primary beam. The angle was measured with a helipot coupled by a gear to the rotating arm. The variations in the gas beam were registered with a second photomultiplier at a fixed position. In order to keep dead-time losses negligible, a "multipulsing technique" was employed[17] and the electrons were recorded with an uppermost countrate of one MHZ. The pulses were discriminated and counted with electronics with an effective pulse pair resolution of 3 nsec due to the multipulsing. The residual gas scattering was recorded by repeating the experiment a second time with a second atomic beam (the first was turned off). This beam was identical to and located close to the first one but care was taken that the electron beam and atomic beam did not come in contact with each other.

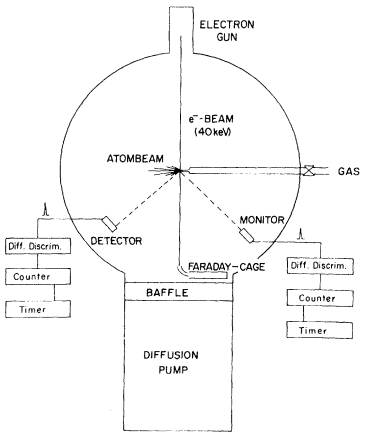

FIG. 2. Diagram of the electron scattering apparatus.

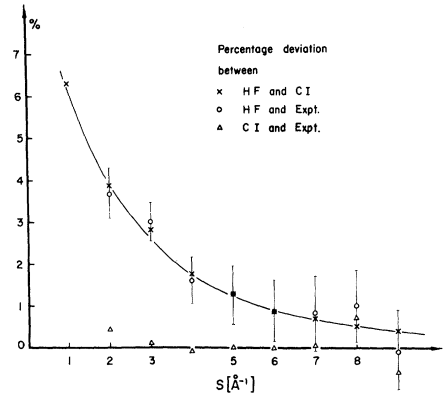

FIG. 3. Comparison between HF and CI calculated scattered intensities and HF and the experimental intensity. ×: $100[I_{\text{total}}(\text{HF}) - I_{\text{total}}(\text{CI})/I_{\text{total}}(\text{HF})]$; O: $100[I_{\text{total}}(\text{HF}) - I_{\text{total}}(\text{expt})]/I_{\text{total}}(\text{HF})$; Δ: $100[I_{\text{total}}(\text{CI}) - I_{\text{total}}(\text{expt})]/I_{\text{total}}(\text{HF})$.

IV. RESULTS

In Fig. 3, the comparisons between the theories and the measurements are shown. The crosses represent the percentage deviation of HF and CI

scattered intensities with respect to the HF values. The circles represent the same quantity with the CI values replaced by the measured intensities. The triangles represent the percentage deviations between CI values and experimental ones with respect to the HF values. The matching factor between theory and experiment was obtained by the following procedure. For each integer s value the ratios of measured intensity and calculated intensities were determined. It was found that the ratios employing CI theoretical intensities were constant to within nearly 0.4%, while the ratios with HF values had larger deviations which varied in a definite manner with increasing s. The constant factor obtained in the CI comparison was then used as the matching factor. The constancy of the ratio in the CI case is a strong indication that the first Born approximation is a valid assumption within the investigated angular range, accelerating voltage and the experimental uncertainties involve. A comparison of the scattered intensities with the first Born approximation for elastic scattering and partial-wave elastic scattering factors showed a variation about a mean value of 0.50% with a maximum at $s = 8$. After the correction of the experimental values for the variation between the first Born approximation and the partial-wave results, the constant ratios deviated from the mean value by less than 0.3%.

Note that there are good physical reasons for suspecting that the Born treatment of the inelastic scattering is superior to the same treatment of the elastic scattering.[18] The uncertainities in the measurement are given as veritical bars in the bottom graph of Fig. 3. The total intensity was recorded with a statistical error of 0.03%, the monitor countrate was recorded to 0.05%. The total background intensity was less than 10% of the scattered intensity at all scattering angles used in this work. The current integrator had an accuracy of 0.1% and was the major source of the uncertainty in I. Unfortunately, the helipot used to determine the scattering variable s had a linearity of only 0.25%. The vertical error bars in Fig. 3 mainly reflect this source of error. It is likely in view of the good agreement between theory and experiment that the manufacturer's stated linearity of his potentiometer is on the conservative side.

V. CONCLUSION

With the agreement between the measurement and the theory including correlation effects, it is obvious that the experimental technique of electron scattering provides sufficiently accurate results so that experimental tests of numerical wave functions can be made in a meaningful manner. Furthermore, one should be able to study correlation effects of systems where no CI wave functions are currently available to an accuracy of at least 20% in the intensity deviations from the HF value. We feel that it should be fairly easy to increase the accuracy of this experiment by at least a factor of 3–4. Limitations upon interpretation of the scattering data from a breakdown of the first Born scattering theory are not yet completely known. The present study indicates that these approximations are exceedingly good. The most serious problems so far encountered occur in the elastic intensity and suggest that studies of the inelastic scattering by use of velocity analyzers might be fruitful.

It is important to note that the failure of the Born approximation at a fixed incident energy depends only on the size of the atom (atomic number).[6] This means that if a certain accuracy level can be obtained in the interpretation of the scattering data for an atom of atomic number Z then at least this accuracy can be obtained in analyzing the results of experiments on smaller atoms or simple molecules containing only the same or smaller atoms. This is in contrast to the theoretical approach where each new particle introduces additional complications.

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Deexcitation of Helium 2^1S and 2^3S Atoms in Fast Collisions with Normal Helium Atoms*

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Cross sections for deexcitation of helium 2^1S and 2^3S atoms in collisions of a helium metastable atomic beam with normal helium atoms have been measured in the laboratory energy range 150–2200 eV. The singlet cross sections are from 20 to 75% larger than the triplet cross sections. Both cross sections were found to obey the general relationship $Q^{1/2}=a-b\ln v$ with an oscillatory structure superimposed upon this monotonic velocity dependence. The magnitude of the triplet cross sections compare favorably with calculated values of the cross section for the symmetric excitation-transfer reaction between 2^3S and 1^1S atoms.

INTRODUCTION

The interaction between metastable and normal helium atoms has received considerable attention because of the repulsive barriers in the interaction potentials at intermediate values of the internuclear separation, and because the He_2 system is simple enough to allow a meaningful detailed comparison between experimental and theoretical data on the interaction of a metastable and a ground-state atom.

There have been several theoretical determinations of potentials for the interaction between normal and metastable helium atoms.[1–5] Total cross sections for scattering,[6,7] diffusion,[8–10] and excitation transfer[11] of 2^3S helium atoms in normal helium have been measured at thermal energies. Experimental results at thermal energies have also been used to make adjustments in the $^3\Sigma_u^+$ and $^3\Sigma_g^+$ potentials of He_2.[8,12] The theoretical potential curves for the interaction of normal and metastable helium atoms have been used to calculate diffusion and excitation-transfer cross sections for 2^1S and 2^3S atoms in their parent gas.[8,12–14] Utterback[15] has observed a resonance in the production of metastable helium atoms in charge-transfer collisions between He^+ and He near threshold. Measurements of cross sections for deexcitation of fast (100–1000 eV) metastable helium atoms have been determined from Penning ionization measurements (where there is no selection between singlet and triplet states).[16] However, no previous measurements of cross sections for production of, excitation by, or deexcitation of 2^3S or 2^1S helium atoms have been carried out at higher than thermal energies or by using molecular beam techniques.

We have measured the cross sections for deexcitation of helium atoms in the 2^1S and 2^3S states in fast (150–2200 eV) collisions with normal helium atoms. The over-all features of the optical excitation and some preliminary results[17] have been