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Molecular x-ray- and electron-scattering intensities

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Various results concerning molecular x-ray- and electron-scattering intensities are presented. (i) Directional elastic intensities for H_2 and N_2 are calculated and a qualitative explanation for the results is given. (ii) The differences between the usual elastic intensities for x-ray and electron scattering from nonvibrating but freely rotating diatomic molecules, and the fully elastic intensities for scattering from the $J=0$ state are examined for H_2 and N_2. The usual elastic intensities are rigorously shown to be greater than the fully elastic ones and the differences are correctly mimicked by the independent-atom model. (iii) Polarization functions are found to be important in the restricted-Hartree-Fock description of the total and elastic intensities. A counterintuitive ordering of basis-set effects on one- and two-electron properties is found and explained in the case of H_2. (iv) It is shown that, in two-electron systems, a quantity closely related to the Coulson-Neilson Coulomb hole function can be extracted from experimental x-ray-scattering intensities. Both these quantities are displayed for H_2. (v) An analogous procedure in the many-electron case is shown to yield the intracular projection of the statistical pair-correlation density.

I. INTRODUCTION

The Waller-Hartree[1] elastic ($I^{\mathrm{xr}}_{\mathrm{el}}$) and total ($I^{\mathrm{xr}}_{t}$) x-ray-scattering intensities are given by[2,3]

$$I^{\mathrm{xr}}_{\mathrm{el}}(\mu)/I_{\mathrm{cl}}=\langle\, |F(\vec{\mu})|^2\rangle \tag{1}$$

and

$$I^{\mathrm{xr}}_{t}(\mu)/I_{\mathrm{cl}}=N+2K(\mu)\ , \tag{2}$$

where the angular brackets denote the spherical average

$$\langle G(\vec{\mu})\rangle=(4\pi)^{-1}\int G(\vec{\mu})d\Omega_{\vec{\mu}}\ , \tag{3}$$

$\vec{\mu}$ is the momentum transfer, I_{cl} the Thomson factor,[4] N is the number of electrons in the target molecule, and Hartree atomic units are used here and throughout this paper. Moreover, the form factor is given by

$$F(\vec{\mu})=\int\rho(\vec{r})\exp(i\vec{\mu}\cdot\vec{r})d\vec{r} \tag{4}$$

in which $\rho(\vec{r})$ is the one-electron charge density while

$$K(\mu)=\int_0^\infty P(u)j_0(\mu u)du\ , \tag{5}$$

where $j_0(x)=x^{-1}\sin x$ and $P(u)$ is the radial intracule (interelectronic distance) density[5] defined in terms of the spinless electron pair density Γ [with $N(N-1)/2$ normalization] by

$$P(u)=\int\Gamma(\vec{r}_1,\vec{r}_2)\delta(u-|\vec{r}_1-\vec{r}_2|)d\vec{r}_1d\vec{r}_2\ . \tag{6}$$

These x-ray intensities are closely related to the elastic ($I^{\mathrm{ed}}_{\mathrm{el}}$) and total ($I^{\mathrm{ed}}_{t}$) electron-scattering intensities in the first Born approximation.[3] Thus

$$\mu^4I^{\mathrm{ed}}_{\mathrm{el}}(\mu)/I_e=I^{\mathrm{xr}}_{\mathrm{el}}(\mu)/I_{\mathrm{cl}}+\sigma_{\mathrm{ne}}(\mu)+\sigma_{\mathrm{nn}}(\mu) \tag{7}$$

and

$$\mu^4I^{\mathrm{ed}}_{t}(\mu)/I_e=I^{\mathrm{xr}}_{t}(\mu)/I_{\mathrm{cl}}+\sigma_{\mathrm{ne}}(\mu)+\sigma_{\mathrm{nn}}(\mu)\ , \tag{8}$$

where I_e is the characteristic Rutherford constant, and the electron-nuclear (σ_{ne}) and nuclear-nuclear (σ_{nn}) interference terms are given by

$$\sigma_{\mathrm{ne}}(\mu)=-2\sum_A Z_A\mathrm{Re}\langle F(\vec{\mu})\exp(-i\vec{\mu}\cdot\vec{R}_A)\rangle \tag{9}$$

and

$$\sigma_{\mathrm{nn}}(\mu)=\sum_{A,B}Z_AZ_Bj_0(\mu\,|\vec{R}_A-\vec{R}_B|\,) \tag{10}$$

in which the sums are over the nuclei with charges Z_A and position vectors $\vec{R}_A$, and $\mathrm{Re}\langle\cdots\rangle$ denotes the real part of $\langle\cdots\rangle$.

The above elastic intensities relate to the usual experiments where rotational energy differences are unresolved. The appropriate expression for the fully elastic intensity for electron scattering from the $J=0$ state of a diatomic molecule was given recently by Kołos, Monkhorst, and Szalewicz,[6] and the analogous expression in the x-ray case is easily obtained. Thus

$$I^{\mathrm{xr}}_{\mathrm{fel}}(\mu)/I_{\mathrm{cl}}=|\langle F(\vec{\mu})\rangle|^2 \tag{11}$$

and[6]

$$\begin{aligned}\mu^4I^{\mathrm{ed}}_{\mathrm{fel}}(\mu)/I_e&=|\langle F(\vec{\mu})\rangle-\sigma_n(\mu)|^2\\&=I^{\mathrm{xr}}_{\mathrm{fel}}(\mu)/I_{\mathrm{cl}}-2\sigma_n(\mu)\mathrm{Re}\langle F(\vec{\mu})\rangle+[\sigma_n(\mu)]^2\end{aligned} \tag{12}$$

in which

$$\sigma_n(\mu)=\sum_A Z_A j_0(\mu R_A)\ . \tag{13}$$

Various results concerning these molecular x-ray-scattering and high-energy electron-scattering intensities are presented in this paper which is laid out as follows. Methodological details such as integration techniques and descriptions of the wave functions used are outlined in Sec. II. Directional elastic x-ray-scattering intensities for H_2 and N_2 are given in Sec. III which also provides a qualitative understanding of these quantities. In Sec. IV, it is shown mathematically that the usual elastic intensities are not less than the fully elastic ones, and numerical results are presented which indicate that the differences between these intensities can be correctly mimicked by the independent-atom model. Section V deals with basis-set effects on the various intensities. Section VI shows how a quantity closely akin to the Coulomb hole can be obtained from x-ray-scattering intensities for two-electron systems. This is illustrated for H_2 using theoretical intensities. In Sec. VII, it is shown that in many-electron systems, x-ray intensities can be utilized to obtain a quantity that contains a mixture of information about the Coulomb and Fermi holes. The main results are summarized in Sec. VIII.

II. METHODOLOGICAL DETAILS

Vibrational averaging effects[6–8] have been neglected and attention will be restricted to the ground states of H_2 and N_2 at the experimental values of their equilibrium internuclear separations R_e. The self-consistent-field (SCF) wave functions used for H_2 were the double-zeta (DZ) function of Snyder and Basch[9] constructed from $(4s)$ Gaussian-type orbitals (GTO's) contracted to $[2s]$, and the extended-basis (EB) function of Huang *et al.*[10] constructed from $(5s,1p)$ GTO's contracted to $[3s,1p]$. The DZ function of Snyder and Basch[9] constructed from $(10s,5p)$ GTO's contracted to $[4s,2p]$ was used for N_2. Moreover, some of the intensities for the EB function for N_2 constructed from Slater-type orbitals (STO's) by Cade and Wahl[11] are available from the work of Epstein and Stewart.[12]

The internuclear axis is aligned with the polar (z) axis, and the origin is at the center of mass. Hence the $D_{\infty h}$ symmetry of the charge density ensures that $F(\vec{\mu})$ is real, even, and independent of the azimuthal angle. The spherical average (3) simplifies to

$$\langle G(\vec{\mu})\rangle=\int_0^1 G(\vec{\mu})d(\cos\theta)\ , \tag{14}$$

where θ is the polar angle of $\vec{\mu}$. Directional form factors $F(\vec{\mu})$ were computed analytically in the standard manner,[13] and the spherical averages (14) were carried out by Gauss-Legendre quadrature. The radial intracule densities required were taken from our earlier work[14] and the Fourier-Bessel transform (5) was carried out using a numerical technique developed previously by two of us.[15]

III. DIRECTIONAL ELASTIC X-RAY INTENSITIES

The elastic x-ray-scattering intensities for H_2 and N_2 in three directions are shown in Fig. 1. A qualitative understanding can be obtained by noting[16] that $F(\vec{\mu})$ is a one-dimensional Fourier transform of the charge density $\rho(\vec{r})$ projected onto the direction of the scattering vector $\vec{\mu}$. Thus $F(\mu\hat{e}_z)$, the form factor in the bond direction $(\theta=0)$, can be expected to oscillate because the projection of $\rho(\vec{r})$ on the bond axis oscillates. Similarly $F(\mu\hat{e}_x)$, the form factor perpendicular to the bond $(\theta=\pi/2)$, can be expected to be diffuse because the projection of $\rho(\vec{r})$ onto the x (or y) axis is sharply peaked. A sharper and semi-quantitative understanding is achieved with the help of the independent-atom model[3] (IAM) which assumes that the molecular density is the simple sum of the spherically averaged atomic densities centered at the equilibrium positions of the pertinent nuclei. For a homonuclear diatomic A_2 with the origin at the center of mass and the internuclear axis aligned with the polar axis, the IAM predicts

$$\begin{aligned}F_{\mathrm{IAM}}(\vec{\mu})&=2f_A(\mu)\cos(\vec{\mu}\cdot\vec{\mathrm{R}}_A)\\&=2f_A(\mu)\cos[(\mu R_e\cos\theta)/2]\ ,\end{aligned} \tag{15}$$

where $f_A(\mu)$ is the atomic form factor. Thus in the bond direction $\theta=0°$, Eq. (15) reduces to

$$F_{\mathrm{IAM}}(\mu\hat{e}_z)=2f_A(\mu)\cos(\mu R_e/2) \tag{16}$$

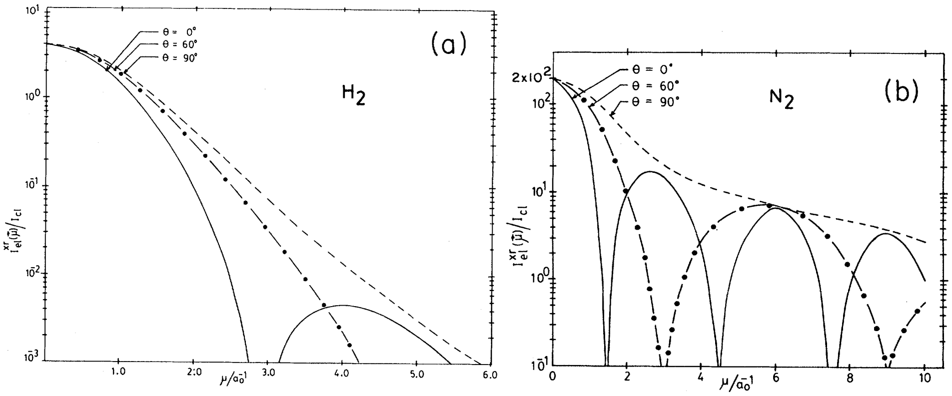

FIG. 1. Elastic x-ray-scattering intensities in three directions. Bond direction corresponds to $\theta=0°$.

and in a direction orthogonal to the bond $\theta=\pi/2$, it yields

$$F_{\rm IAM}(\mu\hat{e}_x)=2f_A(\mu)\ . \tag{17}$$

Since the form factors for the H and N atoms are monotonically decreasing functions,[17] the IAM expressions (15)–(17) are in harmony with Fig. 1.

IV. DIFFERENCES BETWEEN ELASTIC AND FULLY ELASTIC INTENSITIES

The differences between the elastic and fully elastic x-ray- and electron-scattering intensities are shown in Fig. 2. The Schwarz inequality enables one to conclude that

$$I^{\rm xr}_{\rm el}(\mu)\ge I^{\rm xr}_{\rm fel}(\mu)\ , \tag{18a}$$

and

$$I^{\rm ed}_{\rm el}(\mu)\ge I^{\rm ed}_{\rm fel}(\mu)\ , \tag{18b}$$

where equality holds in the case that $F(\vec{\mu})$ is spherically symmetric. Naturally, Fig. 2 is in accordance with inequalities (18), with greater differences being seen in N_2 with its more anisotropic $F(\vec{\mu})$. The differences are greater in the electron-scattering case and do not fall off with increasing μ as they do in the x-ray case.

Since the effect of rotation is primarily controlled by the molecular geometry which is properly accounted for by the IAM, one might expect[6] that these differences between elastic and fully elastic intensities would be correctly predicted by the IAM expressions that are applicable to homonuclear diatomics:

$$[I^{\rm xr}_{\rm el}(\mu)-I^{\rm xr}_{\rm fel}(\mu)]/I_{\rm cl}=[f_A(\mu)]^2[g(\mu R_e)]\ , \tag{19}$$

$$\mu^4[I^{\rm ed}_{\rm el}(\mu)-I^{\rm ed}_{\rm fel}(\mu)]/I_e=[f_A(\mu)-Z_A]^2 g(\mu R_e)\ , \tag{20}$$

in which

$$g(x)=2+2j_0(x)-4[j_0(x/2)]^2\ . \tag{21}$$

The IAM differences are also shown in Fig. 2 and it can be seen that they do mimic the true molecular differences. Note that $g(x)\sim ax^4$ for small x, and $g(x)\rightarrow 2$ in an oscillatory fashion as $x\rightarrow\infty$. Moreover,[2] the atomic form factor $f_A(\mu)\sim Z_A+b\mu^2$ for small μ, and $f_A(\mu)\sim d\mu^{-4}$ for large μ. Thus the IAM difference (19) in the x-ray case increases as μ^4 at small μ and decays to 0 as μ^{-8} at large μ. Such behavior is seen in Figs. 2(a) and 2(c). In the case of electron scattering, the IAM difference (20) increases as μ^8 at small μ and, because of the nuclear-nuclear interference contributions, it approaches $2Z_A^2$ in an oscillatory manner at large enough μ. In Figures 2(b) and 2(d), the differences indeed approach 2 and 98, respectively, for H_2 and N_2.

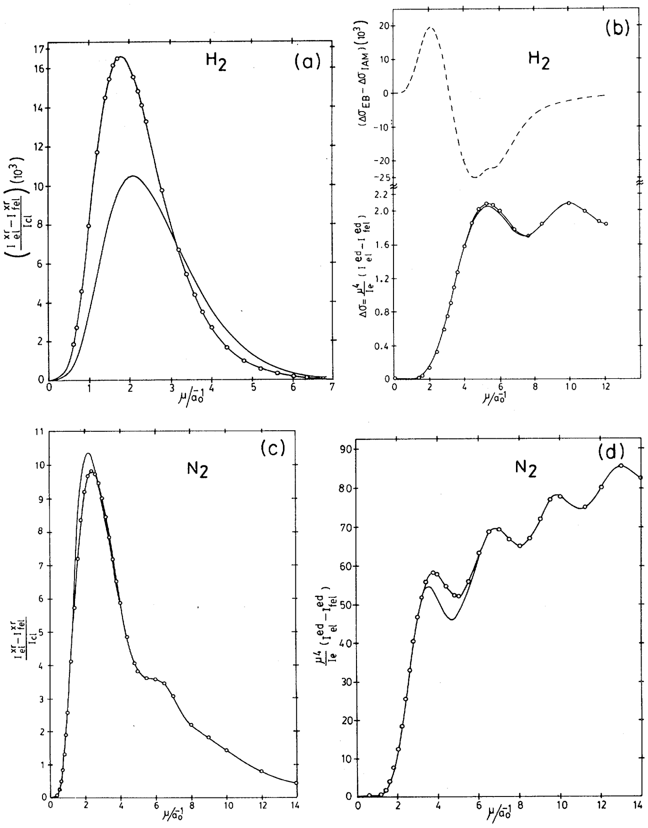

FIG. 2. Differences between the elastic and fully elastic x-ray- and electron-scattering intensities for H_2 and N_2 (note the changes in scale). ——, calculated using molecular wave functions; —○—○, calculated in the IAM. (b) — — — represents the double difference ($\Delta\sigma_{\rm EB}-\Delta\sigma_{\rm IAM}$).

V. BASIS-SET EFFECTS

Figure 3(a) shows the differences between the $I^{\rm xr}_{\rm el}(\vec{\mu})/I_{\rm cl}$ values computed from the EB and DZ functions for H_2. Clearly, polarization functions are needed to obtain accurate results at the restricted Hartree-Fock (RHF) level. This effect is most pronounced in the bond direction. The volume element $\sin\theta$ damps this effect in the spherically averaged $I^{\rm xr}_{\rm el}(\mu)/I_{\rm cl}$ as illustrated in Fig. 3(b). The latter also shows basis-set effects on $I_t^{\rm xr}(\mu)/I_{\rm cl}$ and $\sigma_{\rm ne}(\mu)$. Of course, the sum of the basis-set effects on $\sigma_{\rm ne}$ and the x-ray intensities constitute the basis-set effects on the corresponding electron intensities [cf. Eqs. (7) and (8)]. Figure 3(b) indicates that in H_2 basis-set effects on the one-electron property $I^{\rm xr}_{\rm el}$ are about twice as large as those on the two-electron property $I_t^{\rm xr}$. This runs counter to ones intuition until it is realized that it is an artifact of the RHF approximation for the ground state of a two-electron system. In this very special case one has

$$\Gamma_{\rm HF}(\vec{r}_1,\vec{r}_2)=|\phi(\vec{r}_1)\phi(\vec{r}_2)|^2=\rho_{\rm HF}(\vec{r}_1)\rho_{\rm HF}(\vec{r}_2)/4\ , \tag{22}$$

where $\rho(\vec{r})=2|\phi(\vec{r})|^2$ is the RHF charge density arising from the RHF orbital $\phi(\vec{r})$. It follows that, for a two-electron system described by a RHF wave function,

$$I_t^{\rm xr}(\vec{\mu})/I_{\rm cl}=2+\tfrac{1}{2}I^{\rm xr}_{\rm el}(\vec{\mu})/I_{\rm cl} \tag{23}$$

and, consequently,

$$I^{\rm xr}_{\rm el}(\vec{\mu},B_1)-I^{\rm xr}_{\rm el}(\vec{\mu},B_2)=2[I_t^{\rm xr}(\vec{\mu},B_1)-I_t^{\rm xr}(\vec{\mu},B_2)]\ , \tag{24}$$

where B_1 and B_2 denote two different basis sets. Figure 3(b) shows exactly the behavior predicted by Eq. (24). Naturally, this behavior does not persist for many-electron systems even in the RHF approximation. Figure 3(c)

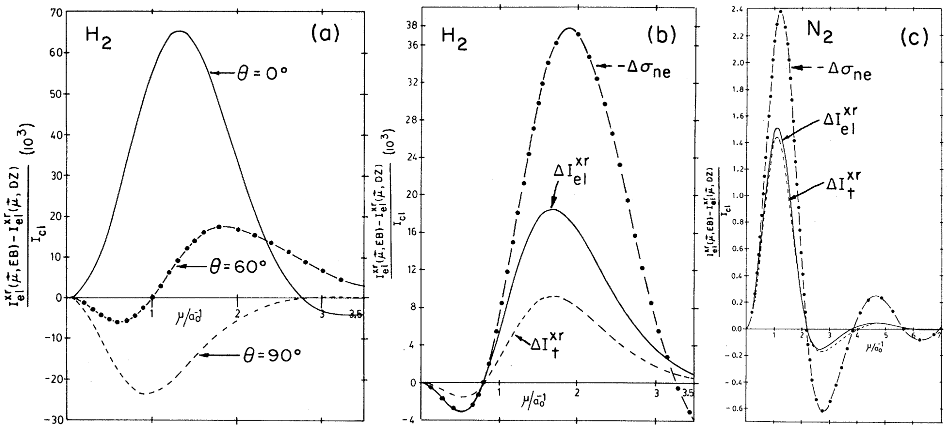

FIG. 3. Basis-set effects on various intensities. (Note the changes in scale.)

shows that, in line with ones intuition, basis-set effects on I_t^{xr} are roughly equal to those on I_{el}^{xr} for N_2. Evidently polarization functions are needed to obtain a RHF level description of these intensities for N_2. This agrees with the work of Hirota, Terada, and Shibata[18] who found that polarization functions were necessary to obtain accurate RHF values of the elastic electron-scattering intensity for N_2 but not for H_2O. For all practical purposes, the basis-set effects on the fully elastic intensities are the same as those for the usual elastic intensities.

VI. COULOMB HOLES FOR TWO-ELECTRON SYSTEMS

It has long been known[2,3] that experimental values of $K(\mu)$, trivially obtainable from experimental values of $I_t^{xr}(\mu)$ and Eq. (2), can yield an experimental radial intracule density through the inverse of Eq. (5):

$$P(u)=(2u^2/\pi)\int_0^\infty \mu^2 K(\mu) j_0(\mu u)\,d\mu \ . \tag{25}$$

This $P_{ex}(u)$ [where the subscript ex designates experiment or exact as appropriate] could then be used along with a calculated RHF $P_{HF}(u)$ to construct the Coulomb hole function of Coulson and Neilson:[19]

$$\Delta P(u)=P_{ex}(u)-P_{HF}(u) \ . \tag{26}$$

In the special case of two-electron systems, the simple structure of the RHF pair density (22) makes it possible to obtain a quantity closely akin to the Coulomb hole (26) by a direct inversion of purely experimental or correlated values of the elastic and total x-ray-scattering intensities. If one writes the exact analog of the RHF expression (22) as

$$\Gamma_{ex}(\vec r_1,\vec r_2)=\rho_{ex}(\vec r_1)\rho_{ex}(\vec r_2)/4+c(\vec r_1,\vec r_2) \tag{27}$$

then the exact analog of the RHF expression (23) becomes

$$\begin{aligned} I_t^{xr}(\vec\mu)/I_{cl} &= 2+\tfrac{1}{2}I_{el}^{xr}(\vec\mu)/I_{cl} \\ &\quad +2\int c(\vec r_1,\vec r_2)\exp[i\vec\mu\cdot(\vec r_1-\vec r_2)]\,d\vec r_1 d\vec r_2 \ . \end{aligned} \tag{28}$$

It follows that the quantity

$$\bar c(u)=(u^2/\pi)\int_0^\infty \mu^2 \Delta I(\mu) j_0(\mu u)\,d\mu \ , \tag{29}$$

where

$$\Delta I(\mu)=I_t^{xr}(\mu)/I_{cl}-2-\tfrac{1}{2}I_{el}^{xr}(\mu)/I_{cl} \tag{30}$$

[is a projection of $c(\vec r_1,\vec r_2)$ defined by

$$\bar c(u)=\int c(\vec r_1,\vec r_2)\delta(u-|\vec r_1-\vec r_2|)\,d\vec r_1 d\vec r_2 \ . \tag{31}$$

From the definition (6), it is apparent that

$$\begin{aligned} \Delta P(u)=\int &[\Gamma_{ex}(\vec r_1,\vec r_2)-\Gamma_{HF}(\vec r_1,\vec r_2)] \\ &\times\delta(u-|\vec r_1-\vec r_2|)\,d\vec r_1 d\vec r_2 \ . \end{aligned} \tag{32}$$

Combining Eqs. (22), (27), and (31) with (32), it obtains that

$$\Delta P(u)=\bar c(u)+\epsilon(u)/4 \ , \tag{33}$$

where

$$\begin{aligned} \epsilon(u)=\int &[\rho_{ex}(\vec r_1)\rho_{ex}(\vec r_2)-\rho_{HF}(\vec r_1)\rho_{HF}(\vec r_2)] \\ &\times\delta(u-|\vec r_1-\vec r_2|)\,d\vec r_1 d\vec r_2 \ . \end{aligned} \tag{34}$$

The Møller-Plesset theorem[20,21] suggests that

$$\rho_{ex}(\vec r)\simeq\rho_{HF}(\vec r) \ . \tag{35}$$

Moreover, only two-electron systems are of concern in the present context, and approximation (35) has been verified computationally for He,[22] H_2,[21,23] and $H_3{}^+$.[24] Hence $\epsilon(u)\simeq 0$ and

$$\Delta P(u)\simeq\bar c(u) \ . \tag{36}$$

It is obvious from the above discussion that, for two-electron systems,

$$\bar c(u)=P_{ex}(u)-P_{HIPM}(u) \ , \tag{37}$$

where $P_{HIPM}(u)$ is the radial intracule density of Henderson's independent-particle model[25] which calls for the lowest energy single determinant wave function that yields the exact charge density $\rho_{ex}(\vec{r})$.

The x-ray intensities that Bentley and Stewart[26] computed from the Davidson-Jones[27] natural orbital expansion of the Kołos-Roothaan[28] wave function were inverted to obtain the $\bar{c}(u)$ shown in Fig. 4. The latter also shows $\Delta P(u)$ based on a $P_{ex}(u)$ obtained by inversion of the Bentley-Stewart[26] I_t^{xr}, and our[14] $P_{HF}(u)$. $\bar{c}(u)$ is seen to be nearly identical to $\Delta P(u)$, and both are qualitatively similar to $\Delta P(u)$ for atomic helium.[19] The radius of the Coulomb hole is $1.675a_0$ in H_2 and $1.06a_0$ in He; the charge moved by Coulomb correlation is $0.070e$ in H_2 and $0.047e$ in He. This shows that Coulomb correlation has a greater range and effect in H_2 than in helium.

VII. A MEASURE OF ELECTRON PAIR CORRELATION IN MANY-ELECTRON SYSTEMS

It is natural to ask whether Eq. (29) can be generalized to many-electron systems. Unfortunately, no measure of the Coulomb hole can be extracted by such a procedure. However, a measure of the combined effects of the Coulomb and Fermi holes can be obtained because Eq. (27) is a special case of our definition[29] of the *statistical* pair-correlation density

$$c(\vec{r}_1,\vec{r}_2)=D_2(\vec{r}_1,\vec{r}_2)-D_1(\vec{r}_1)D_1(\vec{r}_2)\ , \qquad (38)$$

where D_1 and D_2 are the unit normalized one- and two-electron densities, respectively. A little algebra shows that Eqs. (29) and (31) hold, in general, if $c(\vec{r}_1,\vec{r}_2)$ is interpreted via Eq. (38) and ΔI is defined by

$$\begin{aligned}\Delta I(\mu)&=2[I_t^{xr}(\mu)/I_{cl}-N-(N-1)N^{-1}I_{el}^{xr}(\mu)/I_{cl}]\\&\quad\times N^{-1}(N-1)^{-1}\\&=2[S(\mu)-N+N^{-1}I_{el}^{xr}(\mu)/I_{cl}]N^{-1}(N-1)^{-1}\ ,\end{aligned} \qquad (39)$$

where $S(\mu)$ is the incoherent scattering function

$$S(\mu)=I_t^{xr}(\mu)/I_{cl}-I_{el}^{xr}(\mu)/I_{cl}\ . \qquad (40)$$

Thus it is seen that the intracular projection (31) of the statistical pair-correlation density (38) can be obtained from purely experimental data. The nature of the projection (31) precludes the calculation of any statistical correlation coefficients[29–31] from $\bar{c}(u)$. However, an angular correlation coefficient τ for atoms *can* be obtained from experimental intensities as shown recently by one of us.[31] Hence the prescription given here for obtaining $\bar{c}(u)$ from experiment is complementary to the prescription[31] for obtaining τ from experiment.

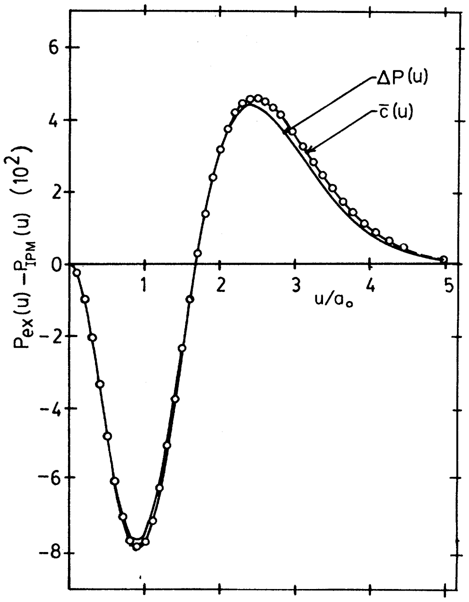

FIG. 4. Coulomb correlation in H_2.

VIII. SUMMARY

The main results presented in this paper are (i) a qualitative explanation, Eq. (15), of the anisotropies of the elastic x-ray intensities shown in Fig. 1; (ii) the rigorous inequalities (18) which state that the usual elastic intensities are not less than the fully elastic intensities; (iii) the numerical demonstration in Fig. 2 that the differences between the elastic and fully elastic intensities can be correctly simulated by the independent-atom model λ; (iv) Fig. 3 which shows the importance of including polarization functions in the basis set when these intensities are calculated; (v) Eqs. (29) and (30) which show how a quantity closely related to the Coulomb hole for a two-electron system may be obtained from x-ray scattering intensities, either theoretical or experimental; (vi) the Coulomb hole for H_2 shown in Fig. 4; and (vii) Eqs. (29) and (39) which show how a measure of the combined effects of the Coulomb and Fermi holes may be obtained from either experimental or theoretical x-ray-scattering intensities.

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proximately equal to that of the incident x ray. The reader is referred to A.J. Thakkar and V. H. Smith, Jr., J. Phys. B 11, 3803 (1978), for a concise summary of the relevant equations.

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