

Li-O-O. The pair of bands at 685 and 730 cm^{-1} , shown in Ref. 1, have an isotopic separation and ratio which agree very well with the theoretical values for ν_3 of a *symmetric* LiO_2 molecule, whether linear or slightly bent. The predicted ν_3 ratio for either $D_{\infty h}$ or C_{2v} (170°) is 1.066; the observed ratio is 1.066 ± 0.002 . If the molecule is linear or only slightly bent ν_1 would have zero or very low infrared intensity. On the other hand, ν_2 could have appreciable intensity. For this reason the 231.1, 243.4 cm^{-1} pair observed in the present work can be assigned to ν_2 of $^7\text{LiO}_2$ and $^6\text{LiO}_2$, respectively. The observed isotope frequency ratio is 1.053 ± 0.004 . The theoretical values are 1.066 for linear geometry, and 1.053 for a 170° model with some assumptions about the magnitude of ν_1 . On this basis it seems safe to conclude that LiO_2 is nearly linear. For the sake of definiteness we assume that the apex angle

of 170° , derived from the structure-sensitive isotopic shift of ν_2 , is correct.

Some estimates of force constants and the bond distance can be made with the help of the arguments already in Ref. 1 for Li_2O . From ν_3 it is found that $(f_r - f_{rr}) = 0.80$ $\text{mdyn}/\text{\AA}$. Since this is much less than $f_r = 1.59$ $\text{mdyn}/\text{\AA}$ for LiO it may be assumed that the interaction constant f_{rr} is large and positive. This would imply, as shown in Ref. 1, that the Li-O bond distance in LiO_2 is appreciably longer than in LiO itself. We assume that $r = 1.65$ \AA in LiO_2 and that $f_{rr} = +0.1$ $\text{mdyn}/\text{\AA}$. On this basis it is found that $\nu_1 = 340$ cm^{-1} . The bending constant $f_\alpha = 0.049$ $\text{mydn}/\text{\AA}$. It is interesting to note that this is much larger than the value found for Li_2O .

The results for LiO , LiO_2 , Li_2O , and Li_2O_2 are summarized in Table II.

Effects of Electron Correlation in X-Ray and Electron Diffraction. IV. Approximate Treatment for Many-Electron Atoms*

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A simple scheme is proposed for predicting effects of electron correlation on intra-atomic electron-electron radial distribution functions and on intensities of x rays scattered by gas atoms. It makes use of a relationship connecting the Coulomb hole function for an electron pair with the corresponding correlation energy. The method is applied to the beryllium atom in its ground state. Results compare favorably with results calculated directly from correlated and Hartree-Fock wavefunctions.

INTRODUCTION

A FUNCTION of special significance in the theory of x-ray scattering by gas atoms is $P(r)$, the intra-atomic radial distribution of electrons with respect to other electrons.¹ This function, unlike the more

familiar radial distribution $D(r)$ of electrons relative to the nucleus, is sensitive to effects of electron correlation. It is related to total x-ray scattering (inelastic plus elastic) by

$$I_{\text{tot}}(\phi) = I_{\text{el}}(\phi) \left[N + \int P(r) \frac{\sin sr}{sr} dr \right] \quad (1)$$

following the notation of Paper I of this series,¹ where $I_{\text{el}}(\phi)$ is the Thomson intensity and N is the number of electrons in the atom.

The influence of electron correlation on $I(\phi)$ and/or $P(r)$ has been calculated for several two-electron systems in earlier papers.^{1,2} The calculations, in which distribution functions and intensities were derived for Hartree-Fock³ and for correlated Roothaan-Weiss⁴

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¹ L. S. Bartell and R. M. Gavin, *J. Am. Chem. Soc.* **86**, 3493 (1964), Paper I; *J. Chem. Phys.* **43**, 856 (1965), Paper II. Note that Eq. (15) of Paper I contains an error. The equation should read

$$\langle \sum_n \bar{V}_{ni} \rangle = -Ze^2 \int_0^\infty \frac{D(r)}{r} dr.$$

It is worth noting in the same reference, also, that according to the definition of $P(r)$, the double sum

$$\sum_i \sum_{i \neq j} \bar{V}_{ij} = e^2 \int_0^\infty \frac{P(r)}{r} dr$$

of Eq. (16) expresses *twice* the average electron-electron potential energy. It is this convention which introduces the factor of 1/4 into Eq. (3) of the present paper.

² C. A. Coulson and A. G. Neilson, *Proc. Phys. Soc. (London)* **78**, 831 (1961); R. F. Curl and C. A. Coulson, *ibid.* **85**, 647 (1965).

³ C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, *Rev. Mod. Phys.* **32**, 186 (1960).

⁴ C. C. J. Roothaan and A. W. Weiss, *Rev. Mod. Phys.* **32**, 194 (1960).

wavefunctions, showed that electron correlation effects followed a regular pattern. The purpose of the present paper is to investigate whether this pattern can be used to predict electron correlation effects in many-electron cases.

METHOD

The proposed scheme for estimating effects of electron correlation on $P(r)$ and $I_{\text{tot}}(\phi)$ makes use of a connection between $P(r)$ and correlation energy. Although extensive information is now available on correlation energies of atoms,^{5,6} very little attention has yet been devoted to $P(r)$. Therefore it seems worthwhile to take advantage of the known correlation energies to estimate correlation effects on $P(r)$ and $I_{\text{tot}}(\phi)$. This may be done without recourse to correlated wavefunctions as outlined below.

The total electronic energy E of an atom is related to the radial distributions $D(r)$ and $P(r)$ according to¹

$$E = \frac{1}{2}\bar{V} = -\frac{1}{2}Z \int \frac{D(r)}{r} dr + \frac{1}{4} \int \frac{P(r)}{r} dr. \quad (2)$$

Since one-electron distributions such as $D(r)$ are virtually the same when calculated by Hartree-Fock (HF) wavefunctions as when calculated by correlated wavefunctions,⁷ the correlation energy E_{corr} for an atom is given very nearly by

$$E_{\text{corr}} \equiv E_{\text{exact}} - E_{\text{HF}} \approx \frac{1}{4} \int \frac{\Delta P(r)}{r} dr, \quad (3)$$

where

$$\Delta P(r) = P_{\text{exact}}(r) - P_{\text{HF}}(r),$$

in which $\Delta P(r)$ represents the shift in $P(r)$ due to electron correlation.

A study of heliumlike systems confirmed that the integrals

$$\left\{ \int \frac{\Delta P(r)}{r} dr \right\} / E_{\text{corr}}$$

were indeed almost identical for all systems. It was revealed that the correction functions $\Delta P(r)/E_{\text{corr}}$ were nearly congruent when plotted against the reduced distance Z^*r , where Z^* is the effective nuclear charge acting on the electron pair. The functions $\Delta P(r)$

resembled the derivatives $-dP(r)/dr$ of the distribution functions themselves.

The simplest way to attempt to generalize the two-electron result to many-electron cases would seem to be as follows. From the Hartree-Fock wavefunction

$$\psi = \mathcal{A}[\phi_1(1)\phi_2(2)\cdots\phi_n(x)]$$

it is possible to calculate the electron-electron distribution function $P(r)$ in terms of the unit normalized average distribution $P(r_{ij})$ using the relation

$$P(r) = N(N-1)P(r_{ij})$$

in which $P(r_{ij})$ is defined by

$$P(r_{ij}) = \int \psi^* \psi \frac{d\tau}{dr_{ij}}$$

The $P(r_{ij})$ functions, in turn, may be expressed in terms of a sum

$$P(r_{ij}) = \sum_k \sum_{l \neq k} P_{kl}(r) \quad (4)$$

over all combinations of orbitals in the atom. To each pair function $P_{kl}(r)$ corresponds a $\Delta P_{kl}(r)$ function which, we assume, is of the characteristic shape found in Paper II. This function is completely specified when its radial and vertical scale factors are assigned. For a given electron pair kl , the radial scale factor of $\Delta P_{kl}(r)$ is adjusted to make its crossover point occur at the maximum of $P_{kl}(r)$. The vertical scale factor is established by setting

$$\frac{1}{4} \left[\int \frac{\Delta P_{kl}(r)}{r} dr \right]$$

equal to the known correlation energy of the electron pair. The total effect of Coulomb correlation on $P(r_{ij})$ may then be obtained by summing the $\Delta P_{kl}(z)$ over all electron pairs. The corresponding shift ΔI_{tot} in the total x-ray intensity is deduced from

$$\frac{I_{\text{tot}}}{I_{\text{el}}} = \int \Delta P(r) \frac{\sin sr}{sr} dr. \quad (5)$$

While such a scheme may fail to predict the correlation correction with great accuracy in complex atoms, it is hard to see how it can be grossly in error. A test of this scheme is afforded by beryllium for which both Hartree-Fock and correlated wavefunctions were available at the time the present work was initiated.

The calculation of $P(r)$ from a correlated wavefunction is much simpler for some forms of wavefunctions than for others. A particularly convenient form to treat is a configuration-interaction function con-

⁵ E. Clementi, J. Chem. Phys. **38**, 2248 (1963); **39**, 175 (1963); **42**, 2783 (1965); **44**, 3050 (1966).

⁶ D. F. Tuan and O. Sinanoğlu, J. Chem. Phys. **41**, 2677 (1964).

⁷ L. Brillouin, Actualites Sci. Ind. No. 159 (1934); J. Goodisman and W. Klemperer, J. Chem. Phys. **38**, 721 (1963); M. Karplus and H. J. Kolker, *ibid.* **38**, 1263 (1963).

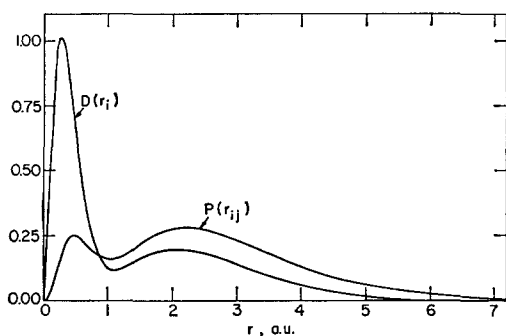


FIG. 1. Electron-nuclear $D(r_i)$ and electron-electron $P(r_{ij})$ radial distribution functions for the beryllium atom calculated from a configuration-interaction wavefunction of Boys. Both $D(r_i)$ and $P(r_{ij})$ curves are normalized to unity. The total electron-nuclear $D(r)$ and electron-electron $P(r)$ radial distribution functions may be obtained by multiplying the normalized curves by N and $N(N-1)$, respectively.

constructed from orthonormal basis orbitals, such as the beryllium wavefunction published by Boys.⁸ Let us assume that the wavefunction is of this form, being expressed as a linear combination

$$\psi = \sum_{\alpha} C_{\alpha} D_{\alpha}$$

of determinantal functions D_{α} representing different electronic configurations. The determinants

$$D_{\alpha} = \mathcal{A}[\lambda_1(1) \cdots \lambda_N(N)]$$

are constructed from basis spin orbitals obeying the orthogonality relation

$$\int \lambda_i(1) \lambda_j(1) d\tau_1 = \delta_{ij},$$

irrespective of whether λ_i and λ_j occur in the same determinant or not. The expression for $P(r_{ij})$ derived from such a function is

$$P(r_{ij}) = \int \psi^* \psi \frac{d\tau}{dr_{ij}} = \sum_{\alpha} \sum_{\beta} C_{\alpha}^* C_{\beta} \int D_{\alpha}^* D_{\beta} \frac{d\tau}{dr_{ij}}. \quad (6)$$

Terms with $\alpha = \beta$ represent the contribution to $P(r_{ij})$ from the α configuration and can be expressed as a sum

$$P_{\alpha\alpha}(r) = \int D_{\alpha}^* D_{\alpha} \frac{d\tau}{dr_{ij}} = \sum_k \sum_{k \neq l} [P_{kl}(r)]_{\alpha} \quad (7)$$

over all pairs of orbitals in the configuration. For $\alpha \neq \beta$ there are three different cases:

(a) If D_{α} differs from D_{β} in one spin orbital, say λ_m in D_{α} and λ_r in D_{β} , the contribution to $P(r_{ij})$

⁸ S. F. Boys, Proc. Roy. Soc. (London) **A201**, 125 (1950).

becomes

$$\begin{aligned} P_{\alpha\beta}(r) &= \int D_{\alpha}^* D_{\beta} \frac{d\tau}{dr_{ij}} \\ &= \sum_{k \neq m} \left[\int \lambda_k^*(i) \lambda_m^*(j) \lambda_k(i) \lambda_r(j) \frac{d\tau_i d\tau_j}{dr_{ij}} \right. \\ &\quad \left. - \int \lambda_k^*(i) \lambda_m^*(j) \lambda_r(i) \lambda_k(j) \frac{d\tau_i d\tau_j}{dr_{ij}} \right]. \quad (8) \end{aligned}$$

(b) If D_{α} differs from D_{β} in two spin orbitals, say λ_m and λ_n in D_{α} , and λ_r and λ_s in D_{β} , the expression for $P_{\alpha\beta}(r)$ is

$$\begin{aligned} P_{\alpha\beta}(r) &= \int \lambda_m^*(i) \lambda_n^*(j) \lambda_r(i) \lambda_s(j) \frac{d\tau_i d\tau_j}{dr_{ij}} \\ &\quad - \int \lambda_m^*(i) \lambda_n^*(j) \lambda_s(i) \lambda_r(j) \frac{d\tau_i d\tau_j}{dr_{ij}}. \end{aligned}$$

(c) If D_{α} differs from D_{β} in three or more spin orbitals, $P_{\alpha\beta}(r) = 0$. Equation (6) may be rewritten, then, as

$$P(r_{ij}) = \sum_{\alpha} \sum_{\beta} C_{\alpha}^* C_{\beta} P_{\alpha\beta}(r)$$

and, for spherically symmetric systems, the method of Coulson and Nielson² may be used to evaluate the $P_{\alpha\beta}(r)$.

RESULTS

Distribution functions for the ground state of beryllium were calculated from an analytical self-consistent-field (SCF) wavefunction of Roothaan, Sachs, and Weiss³ and from a configuration-interaction

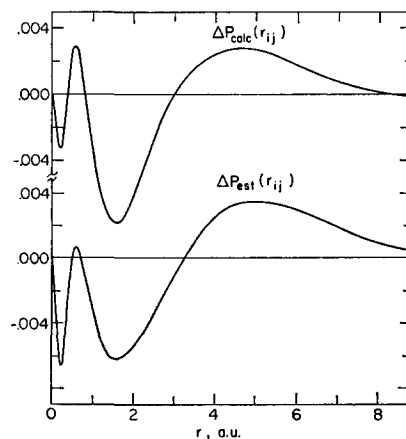


FIG. 2. Calculated and estimated correlation shifts in $P(r_{ij})$ for the beryllium atom. The function $\Delta P_{\text{calc}}(r_{ij})$ was calculated from atomic wavefunctions and $\Delta P_{\text{est}}(r_{ij})$ was estimated employing the scheme outlined in the text.

(CI) function of Boys⁸ which accounts for 50% of the correlation energy. The accuracy of the calculations was checked by determining the total electronic energy utilizing Eq. (2). For both wavefunctions the energy agreed exactly with the published value. In Fig. 1 are plotted the electron-electron $P(r)$ and electron-nuclear $D(r)$ functions derived from the wavefunction of Boys. Shown in Fig. 2 are $\Delta P_{\text{calc}}(r)$, defined by

$$\Delta P_{\text{calc}}(r) = P_{\text{CI}}(r) - P_{\text{SCF}}(r),$$

and $\Delta P_{\text{est}}(r)$, the correlation correction function estimated by the scheme of the previous section.

The actual reference function $\Delta P(Z^*r_{12})$ upon which $\Delta P_{\text{est}}(r)$ was based is the function derived in Paper II for the Be^{++} ion. In Table I are listed the data used to set the radial and vertical scale factors of the components in $\Delta P_{\text{est}}(r)$. These data include estimates of correlation energies associated with various electron pairs in the beryllium atom⁶ and the positions of the maxima of the pair distribution curves $P_{1s,1s}$, $P_{2s,2s}$, $P_{1s,2s}$ calculated from the SCF orbitals

Figure 3 illustrates the calculated (CI-SCF) and estimated [from $\Delta P_{\text{est}}(r)$] shifts in $I_{\text{tot}}(\phi)$ arising from electron correlation. The curves were obtained by application of Eq. (5).

DISCUSSION

The simple scheme proposed in the present paper correctly predicts the main features of the $\Delta P(r)$ and $\Delta I_{\text{tot}}(\phi)$ functions for Be. While the base lines of the

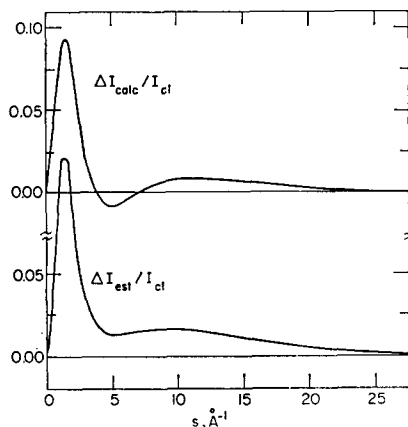


FIG. 3. Shifts in the total intensity due to electron correlation. ΔI_{calc} and ΔI_{est} were derived from the corresponding shifts in $P(r)$ illustrated in Fig. 2.

TABLE I. Pair-correlation energies ϵ_{ij} and radial values r_{max} for the maxima of the pair distribution functions in beryllium.

Pair	ϵ_{ij} (eV) ^a	r_{max} (a.u.)
1s-1s	-1.196	0.44
1s-2s	-0.176	2.10
2s-2s	-1.195	3.25

^a Reference 6.

predicted and calculated curves disagree somewhat, the maxima and minima are roughly coincident. It is not clear whether the discrepancy between the curves is due more to inaccuracies in the proposed scheme for estimating $\Delta P(r)$ or to the inaccuracy of the correlated wavefunction which accounts for only 50% of the correlation energy. Recently, some considerably more accurate wavefunctions for Be have become available which can provide a more rigorous test.⁹

We may conclude, provisionally, that the present scheme works at least approximately for predicting effects of Coulomb correlation on $P(r)$ and $I_{\text{tot}}(\phi)$. Even though the reference Coulomb hole function is based on K -shell behavior, the generalization seems to apply to the L shell also. Individual $P_{kl}(r)$ functions are more diffuse than $D_k(r)$ functions, and hence do not exhibit as striking variations in form. Perhaps this diffuseness tends to minimize the individuality of the $\Delta P_{kl}(r)$ contributions.

The present results also strengthen our earlier conjecture that the largest relative effects on x-ray scattering may be expected for shells of smallest effective nuclear charge and greatest radius in the atom. Results of applying the present treatment to a system with many more electrons, namely to neon, may be found in Paper III of this series.¹⁰ The estimated $\Delta I_{\text{tot}}(\phi)$ should provide a useful indication of how accurate an experiment must be to yield a $P(r)$ function with better than Hartree-Fock accuracy. Although current techniques¹¹ seem to have approached this precision for lighter atoms, it is unlikely that critical experimental tests will soon be made of even such crude theories of correlation effects as the present scheme.

⁹ K. J. Miller and K. Ruedenberg, J. Chem. Phys. **43**, S88 (1965); A. Weiss, Phys. Rev. **122**, 1826 (1961).

¹⁰ R. M. Gavin, Jr., and L. S. Bartell, J. Chem. Phys. **44**, 3687 (1966).

¹¹ D. R. Chipman and L. D. Jennings, Phys. Rev. **132**, 728 (1963).