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The Analysis of Electron Pair Distribution Functions in Molecules

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Electron pair distribution functions are analyzed for a variety of SCF+CI wavefunctions, for a range of simple molecules. The statistical correlation between electrons of like spin introduced by the antisymmetry requirement on the many-electron wavefunction is contrasted with the manner in which unlike-spin electron correlation is introduced through the inclusion of configuration interaction.

Key words: Electron pair distribution

1. Introduction

The single electron distribution function, or electron probability density, is the subject of a vast literature in quantum chemistry (see, for example, the recent review article by Bader [1]), and a text [2] is devoted entirely to electron density plots for wavefunctions of SCF type. Much less attention has been paid to the two-electron distribution function, and in particular to its components for pairs of electrons with like and unlike Z-components of spin angular momentum. The analysis of such distribution functions has been confined in the main to two-electron systems, where extremely accurate wavefunctions are available, with particular emphasis on the form of the Fermi [3–5] and Coulomb [6, 7] correlation holes. Similar calculations are also available for the H_6 ring system [8] and for two-, three- and four-electron ions [9].

The present investigation is designed to study the behaviour of these pair distribution functions in many-electron systems, using the conventional approximation

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of a single-determinant (SCF) wavefunction, supplemented by the inclusion of (extensive) configuration interaction. The information provided by such an analysis both reinforces and complements that available from an examination of the single electron distribution function [1] and from spatially-averaged expectation values, particularly from well-studied one-electron properties such as dipole moment [10].

The manner in which Fermi and Coulomb correlation (for electrons of like and unlike spin, respectively) is introduced by the various approximations currently employed in quantum chemistry is fundamental to our understanding of the correlation problem itself, and may be instrumental in suggesting schemes for the construction of improved wavefunctions. It is well known [11] that statistical correlation between electrons of like spin is introduced at SCF level by the antisymmetry requirement on the many-electron wavefunction, whereas such correlation is entirely lacking, at this level of approximation, for electrons of unlike spin.

We shall study in this paper the pair distribution functions [12–14], for electrons of like and unlike spin components respectively,

$$P_2^{\alpha\alpha}(\mathbf{r},\mathbf{r}')=\langle\Psi|\sum_{i,j}{}'\delta(\mathbf{r}-\mathbf{r}_i)\delta(\mathbf{r}'-\mathbf{r}_j)[\tfrac{1}{4}+S_z(\sigma_i)S_z(\sigma_j)]|\Psi\rangle \tag{1}$$

$$\mathbf{P}_2^{\alpha\beta}(\mathbf{r},\mathbf{r}')=\langle\Psi|\sum_{i,j}{}'\delta(\mathbf{r}-\mathbf{r}_i)\,\delta(\mathbf{r}'-\mathbf{r}_j)[\tfrac{1}{4}-S_z(\sigma_i)S_z(\sigma_j)]|\Psi\rangle \tag{2}$$

for a range of SCF + CI calculations on some simple molecules. The prime on the double summation in Eqs. (1) and (2) indicates that the term $i=j$ is to be excluded, and the formulae are valid only for singlet states, with $S=M_s=0$. Using the McWeeny normalization, $N(N-1)$, of the electron pair distribution function, P_2, [12] we note that $P_2^{\alpha\alpha}$ and $P_2^{\alpha\beta}$ will be normalized to $(N/2)(N/2-1)$ and $(N/2)^2$ respectively.

Although it is customary [15, 16] to consider matrix representatives $\mathbf{P}_2$ of $P_2(\mathbf{r},\mathbf{r}')$ within an orbital basis set (i.e. pair population analysis), we shall present our results in the form of pair probability densities for pairs of points $\mathbf{r}$, $\mathbf{r}'$, thus permitting variations to the primitive orbital basis set.

For a single determinant wavefunction, Eqs. (1) and (2) reduce to the simple forms [11, 12]

$$P_2^{\alpha\alpha}(\mathbf{r},\mathbf{r}')=P_1^{\alpha}(\mathbf{r})P_1^{\alpha}(\mathbf{r}')-|P_1^{\alpha}(\mathbf{r};\mathbf{r}')|^2 \tag{3}$$

$$P_2^{\alpha\beta}(\mathbf{r},\mathbf{r}')=P_1^{\alpha}(\mathbf{r})P_1^{\beta}(\mathbf{r}') \tag{4}$$

where $P_1(\mathbf{r};\mathbf{r}')$ is the spinless reduced one-electron density matrix, and $P_1(\mathbf{r})\equiv P_1(\mathbf{r};\mathbf{r})$ is the electron probability density function.

2. Computational Procedure

The pair distribution functions $P_2^{\alpha\alpha}(\mathbf{r},\mathbf{r}')$ and $P_2^{\alpha\beta}(\mathbf{r},\mathbf{r}')$ have been calculated at selected pairs of points in the molecules CH_4, NH_3, H_2O and HCN. The calculations were performed using Dunning's contracted basis sets [17] (as derived from the Huzinaga [18] 9*s*5*p* sets for C, N and O, and the 4*s* set for H) augmented by certain polarization functions, (which allow a more flexible description of the effect of the molecular environment around each atomic centre) with values of exponents chosen from recent calculations in the literature (CH_4 [19], NH_3 [20], H_2O [21]). The Dunning basis sets can be found in an Appendix to his paper [17].

Since many calculations in the literature can, for practical reasons, differ only in the number of contractions within a given set of Gaussian orbitals, the subsequent variations induced in $P_2(\mathbf{r}, \mathbf{r}')$ and its components are of some interest. It would, of course, be desirable to compare the results from calculations with distinct basis sets, but this is a computationally expensive procedure, since exponent optimization must first be performed.

In view of the related nature of our basis sets, we shall employ the convenient shorthand notation *spd*. . ./*spd*. . ./. . . where each group refers to the number of contracted basis functions of *s*, *p*, *d*, . . . symmetry respectively on a particular atom, and the groups refer to inequivalent atoms listed in order of decreasing atomic number, e.g. 421/2 for H_2O refers to the contracted set of (4*s*-, 2*p*-, 1*d*-) functions on C, and 2*s*-functions on H. The SCF calculations are routine [22, 23], the SCF+CI calculations employ a previously-described [24] symbolic matrix element scheme involving spin-eigenfunctions, together with an efficient transformation package [25] for both matrix elements and distribution functions developed by one of the present authors (C.N.M.P.), and the computational details can be found elsewhere [26].

The CI calculations included all possible single excitations of the type $(i) \rightarrow (u)$, and all double excitations of the type $(ii) \rightarrow (uu)$, together with a selection of configurations of types $(ii') \rightarrow (uu)$, $(ii) \rightarrow (uu')$, $(ii') \rightarrow (uu')$, where i, i' refer to members of the set of occupied SCF orbitals, and u, u' refer to members of the corresponding set of virtual orbitals. This selection was carried out using the virtual orbital energies as a guide, such that, once all excitations of the type $(i) \rightarrow (u)$, $(ii) \rightarrow (uu)$ were included, all double excitations from the valence orbitals were incorporated up to and including some "terminal" virtual orbital, v, which could then be varied. This technique produces a large number of interacting configurations in general.

3. Discussion of Results

Although the pair distribution functions $P_2^{\alpha\alpha}$ and $P_2^{\alpha\beta}$ were evaluated at selected pairs of points in a range of simple molecules, the observed trends were found to be similar in each case [26] and only one molecule will be considered here. We shall present a range of results for the $^1A_1$ ground state, for C_{2v} symmetry, and equilibrium geometry [27], of the H_2O molecule.

Table 1 lists the various CI calculations, together with their energies, constituent basis sets, and number of configurations in the expansion. The various SCF energies are omitted since they can be inferred from the tabulated values of E_{CI} and $\Delta E = E_{CI} - E_{SCF}$. It should be noted that the configurations refer to eigenfunctions

Table 1. Data on CI calculations on H_2O

CI calculation	E_{CI}/hartree[a]	ΔE/hartree ($=E_{CI}-E_{SCF}$)	Basis	No. of configurations	No. of interacting terms
1	-76.134	-0.126	32/2	861	115171
2	-76.146	-0.137	42/2	855	106540
3	-76.193	-0.159	421/2	964	129746
4	-76.208	-0.174	421/2	1201	195841
5	-76.184	-0.150	421/2	1226	195341
6	-76.205	-0.171	421/2	1249	229069
7	-76.213	-0.179	421/2	1291	235144
8	-76.198	-0.160	422/2	1295	239960

[a] The estimated Hartree–Fock limit is $-76.067(5)$ hartree [28, 29].

of the operator S^2, and hence the number of constituent determinants in the expansion is considerably greater than the listed number of configurations.

The configurations were chosen as described in the previous section, except for CI5, which included every excitation type originating with the $1a_1$ orbital (a "cut-off" virtual orbital, v, of slightly lower energy was necessary) and CI6, which involved the "frozen core" approximation, in which all excitations (single and double) from the $1a_1$ orbital were excluded.

The following points should be noted from Table 1:

a) For the calculations CI3, CI4 and CI7, with a fixed primitive SCF orbital basis, the energy decreases as the number of configurations increases. Calculation CI5 reflects energetically the increased number of unfavourable excitations from the core orbital at the expense of the valence orbitals, while calculation CI6 (the "frozen-core" calculation) is distinguishable from CI4 by having a marginally higher energy for a larger number of configurations (and an accompanying larger number of interacting terms of the Hamiltonian matrix).

b) Calculation CI8, which has a higher energy than calculations CI4, CI6 and CI7, reflects the extra computational effort (it contains the largest number of configurations) required to produce comparable energies when using a larger basis set.

c) All calculations are below the Hartree–Fock limit [28, 29] recovering from between 18% (CI1) to 40% (CI7) of the correlation energy (of -0.370 hartree).

For convenience in the discussion of the pair distribution functions, we include (Table 2) values of the electron probability density on the atomic centres for the various SCF and SCF + CI calculations. These values reproduce the familiar result that $P_1(\mathbf{r})$ is adequately described at SCF level. The CI calculations [26] show that $P_1(\mathbf{r})$ decreases from the corresponding SCF values in the bonding region, and this is in direct contrast to the effect on $P_1(\mathbf{r})$ of including polarization functions to the basis at SCF level. This result indicates that the inclusion of even extensive configuration interaction cannot compensate for the inadequacy of the basis set, and agrees with the conclusions of Green [10] based on dipole moment calculations.

Table 3 lists some values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ for both the SCF and SCF + CI calculations. The SCF values, in accord with Eq. (4), are simply products of the values of the electron probability density at the points concerned, since electrons of unlike spin are statistically uncorrelated at SCF level. A direct consequence of this result is that the probability density of observing simultaneously two electrons at two points related to each other by symmetry is identical to the corresponding probability density for two electrons of opposite spin at either point. This is borne out in Table 3 by the equality of the SCF values of $P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_H)$ and $P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_{H'})$. Note that this effect disappears on performing the CI calculations when $P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_H)$ is reduced considerably from its SCF value, whereas $P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_{H'})$ is virtually unchanged.

Although $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r})$ is relatively unaffected by change of basis at SCF level (in line with variations in $P_1(\mathbf{r})$ – see Eq. (4)) there is a marked variation in values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r})$ for different basis sets (excluding CI6, which will be discussed below). We see in general that the statistical correlation introduced by the inclusion of configuration interaction, for electrons of unlike spin, decreases as the size of the basis increases, since the values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r})$ increase. We note in particular that, for the 421/2 basis, CI4 and CI7 give almost identical results for $P_2^{\alpha\beta}(\mathbf{r}_O, \mathbf{r}_O)$, despite the fact that there is a considerable disparity in the number of configurations (cf. Table 1). This suggests that the amount of Coulomb correlation introduced by the method of configuration interaction is basis-set dependent, decreasing as the size of the basis set increases.

Table 2. Values of $P_1(\mathbf{r})/a_0^{-3}$ at selected points in H_2O

a) SCF values

Basis	$P_1(\mathbf{r}_O)$	$P_1(\mathbf{r}_H)$
32/2	295.135	0.4132
42/2	295.051	0.4147
421/2	294.925	0.3967
422/2	294.925	0.3967

b) CI values

CI calculation	$P_1(\mathbf{r}_O)$	$P_1(\mathbf{r}_H)$
1	295.149	0.4208
2	295.208	0.4220
3	294.998	0.4002
4	295.025	0.4029
5	295.024	0.4027
6	294.960	0.4028
7	295.034	0.4028
8	295.082	0.4103

Table 3. Values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')/a_0^{-6}$ at selected pairs of points in H_2O

a) SCF Values

Basis	$P_2^{\alpha\beta}(\mathbf{r}_O, \mathbf{r}_O)$	$P_2^{\alpha\beta}(\mathbf{r}_O, \mathbf{r}_H)$	$P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_H)$	$P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_{H'})$
32/2	21776.19	30.488	0.0427	0.0427
42/2	21763.74	30.586	0.0430	0.0430
421/2	21745.12	29.318	0.0396	0.0396
422/2	21745.12	29.318	0.0395	0.0395

b) CI values

CI calculation	$P_2^{\alpha\beta}(\mathbf{r}_O, \mathbf{r}_O)$	$P_2^{\alpha\beta}(\mathbf{r}_O, \mathbf{r}_H)$	$P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_H)$	$P_2^{\alpha\beta}(\mathbf{r}_H, \mathbf{r}_{H'})$
1	20255.55	31.127	0.0195	0.0428
2	20404.75	31.224	0.0199	0.0431
3	20638.18	29.537	0.0256	0.0397
4	20647.91	29.767	0.0217	0.0403
5	20641.94	29.747	0.0205	0.0414
6	21745.09	29.758	0.0205	0.0404
7	20649.74	29.764	0.0206	0.0404
8	20822.47	30.305	0.0233	0.0440

Calculation CI6, which corresponds to the "frozen-core" approximation, shows no Coulomb correlation whatsoever at the oxygen atom, in that $P_2^{\alpha\beta}(\mathbf{r}_O, \mathbf{r}_O)$ is unchanged from its SCF value, although the total energy of this calculation is comparable with that of the other calculations using this basis set (see Table 1). This result simply shows that all the correlation effects on the oxygen are attributable to the $1a_1$ orbital, and for a given size of basis, $P_2^{\alpha\beta}(\mathbf{r}_O, \mathbf{r}_O)$ is relatively insensitive to the particular choice of configurations provided all single and double excitations of the type $(i) \rightarrow (u)$, $(ii) \rightarrow (uu)$ respectively are included. It is of interest to note that Rosenberg and Shavitt [30] found that the "frozen-core" approximation had only a slight effect on expectation values, whereas in a related [31] paper on potential energy surfaces, they found that the "frozen core" approximation could significantly affect the quartic potential coefficients, and did not include a "frozen core" in their final CI calculations.

It is apparent from this work that the major effect of the "frozen core" approximation (apart from the reduction in computational effort required in the calculation) is an inadequate description of Coulomb correlation in the vicnity of the heavy atom, and, although it does not show up in the calculation of the usual expectation values, it is a serious deficiency in what would otherwise be a reasonably accurate wavefunction.

At large separations of $\mathbf{r}$ and $\mathbf{r}'$, we note from Table 3 that the CI values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ are only slightly ($\sim$2–3%) increased from the corresponding SCF values. This is to be expected since $P_2^{\alpha\beta}$ has a constant normalization in both cases, and the

Table 4. Values of $P_2^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')/a_0^{-6}$ at selected pairs of points in H_2O[a]

a) SCF values

Basis	$P_2^{\alpha\alpha}(\mathbf{r}_O, \mathbf{r}_H)$	$P_2^{\alpha\alpha}(\mathbf{r}_H, \mathbf{r}_{H'})$
32/2	30.362	0.0414
42/2	30.459	0.0417
421/2	29.191	0.0389
422/2	29.191	0.0389

b) CI values

CI	$P_2^{\alpha\alpha}(\mathbf{r}_O, \mathbf{r}_H)$	$P_2^{\alpha\alpha}(\mathbf{r}_H, \mathbf{r}_{H'})$
1	30.967	0.0418
2	31.040	0.0421
3	29.393	0.0391
4	29.588	0.0422
5	29.577	0.0424
6	29.581	0.0421
7	29.589	0.0421
8	30.163	0.0449

[a] $P_2^{\alpha\alpha}(\mathbf{r}, \mathbf{r}) \equiv 0$ (cf. Eq. (3))

effect of configuration interaction is generally to significantly reduce the values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}' = \mathbf{r})$, so that $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ must increase slightly for $\mathbf{r} \neq \mathbf{r}'$ to preserve normalization.

Table 4 lists certain values of $P^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ for both SCF and SCF + CI calculations and we note that, while $P_2^{\alpha\alpha}(\mathbf{r}, \mathbf{r}' = \mathbf{r}) \equiv 0$ (by Eq. (3)), the values of $P_2^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ are only marginally changed from their SCF values, indicating that the additional correlation introduced by configuration interaction over and above the statistical correlation introduced by antisymmetrization at SCF level is negligible for most separations of $\mathbf{r}$ and $\mathbf{r}'$ (and is, of course, zero for $\mathbf{r} = \mathbf{r}'$).

A comparison of Tables 3 and 4 shows that the SCF values of $P_2^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ are consistently smaller than the corresponding values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ and this follows naturally from Eq. (3), in which the positive "interference" term $|P_1^{\alpha}(\mathbf{r}; \mathbf{r}')|^2$ is subtracted from the term $P_1^{\alpha}(\mathbf{r})P_1^{\alpha}(\mathbf{r}')$ $(\equiv P_1^{\alpha}(\mathbf{r})P_1^{\beta}(\mathbf{r}') = P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ in the present instance).

4. Conclusions

Our analysis of the pair distribution functions $P_2^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ and $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ in many-electron systems has provided a detailed breakdown of correlation effects which is not ascertainable directly from an analysis of spatially-averaged expectation values. In particular, we have shown that the absolute values of $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r})$ are determined primarily by the basis set, the amount of Coulomb correlation introduced by configuration interaction decreasing with increasing size of basis set, for calculations of comparable size. The use of the "frozen-core" approximation is such as to inhibit completely the effect of Coulomb correlation at the heavy atom.

The behaviour of short-range correlation effects (Fermi and Coulomb correlation holes) around a reference point has only been referred to briefly here, and will be one subject of a separate analysis [32]. The present analysis, however, has done much to show that the behaviour of the pair distribution functions $P_2^{\alpha\alpha}(\mathbf{r}, \mathbf{r}')$ and $P_2^{\alpha\beta}(\mathbf{r}, \mathbf{r}')$ has an important role to play in the detailed analysis of many-electron wavefunctions in molecules

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