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The doubly-excited state $2p^2 \, ^3P$ for $1 \leq Z \leq 4$: Coulomb holes derived from explicitly correlated wavefunctions
The doubly-excited state $2p^2 \ ^3P$ for $1 \leq Z \leq 4$: Coulomb holes derived from explicitly correlated wavefunctions

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Abstract. Doubly-excited states (DES) of simple atoms involve, by comparison with the ground state, relatively slow moving electrons which should therefore be more responsive to electron correlation. Hence, for the $2p^2 \ ^3P$ state, correlation effects have been analysed in detail in terms of Coulomb holes, partial Coulomb holes and $\langle r_{ij}^n \rangle$ when $1 \leq Z \leq 4$. Comparisons are made with the $1s^2 \ ^1S$ ground state and with the singly-excited state $1s^2 \ ^1P$. As for the lower states, each DES was described by an accurate explicitly correlated wavefunction.

For each $Z$, a similarity of characteristics, but not of scale, is found between the DES results and those for the ground state. The Coulomb holes for the $1s2p \ ^1P$ states have a significantly different shape. The correlation effect for each DES system exceeds that for the corresponding lower states examined here. By comparison with He and the positive ions, the effect for $H^-(2p^2 \ ^3P)$ is massive. The diffuseness of the partial Coulomb hole for $H^-$ enabled us to identify and account for distinct features which, it is felt, will constitute the basic components of correlation diagrams for other atomic 'double-occupancy' states.

1. Introduction

Doubly-excited states (DES) of atomic systems usually autoionize. However, for the $2p^2 \ ^3P$ state when the atomic number $Z$ is small, as considered here, conservation of parity and angular momentum prevents Coulombic autoionization (Drake and Dalgarno 1970). The state is thus rendered metastable. When $Z$ is large and $LS$ coupling breaks down, autoionization of the $2p^2 \ ^3P$ state will then occur (Boiko et al 1977). In addition, for any $Z$, radiative autoionization (Drake 1973, 1974, Nicolaides 1983) can exist whereby the two-electron system emits an electron and a photon, leaving the resulting hydrogen-like ion in its ground state.

The most important decay mechanism of the $2p^2 \ ^3P$ state is the radiative transition to the $1s2p \ ^3P$ state. For helium, a spectral line corresponding to this transition was first observed by Kruger (1930) and was subsequently substantiated theoretically by Wu (1944). Transitions involving the $2p^2 \ ^3P$ state of Li$^+$ and Be$^+$ have also been observed and agree with theory (Buchet et al 1973, Anderson et al 1980). For high-$Z$ systems, this state has been routinely identified in nuclear fusion plasma experiments (Lunney and Seely 1982, Audebert 1984, Bañón et al 1985, Karim and Bhalla 1988). By contrast, when $Z=1$ there is, as yet, no conclusive experimental evidence for the existence of a $2p^2 \ ^3P$ state even though, according to calculation, it is just bound (Jáuregui and Bunge 1979).
The theoretical interest in DES for small $Z$ systems is particularly challenging since their description requires a wavefunction which allows for a high degree of electron correlation. Basically, such wavefunctions may be of an explicit form, involving the interelectronic separation $r_{12}$, or of a configuration-interaction type (see, for example, Drake 1970, Bhatia 1970, Beck and Nicolaides 1978, Jáuregui and Bunge 1979, and references therein). More recently, Drake (1986) has produced a series of extremely accurate explicitly-correlated wavefunctions for $H^-$, He, Li$^+$ and Be$^{2+}$ in the $2p^23P$ state. For each system, the energy convergence achieved by Drake suggests that the energetically best of these Hylleraas-type functions recovers virtually 100% of the correlation energy. Indeed, for Li$^+$ and Be$^{2+}$, no energetically superior wavefunctions are known for this state. The inherent importance of electron correlation in DES, coupled with the excellence of these wavefunctions, makes an analysis of the correlation effects in the $2p^23P$ states of $H^-$, He, Li$^+$ and Be$^{2+}$ both desirable and feasible. To obtain general comparisons with the ground states, and also with the singly-excited $1s2p3P$ states, we have determined the corresponding Coulomb holes, $\Delta f(r_{12})$ versus $r_{12}$, and partial Coulomb holes, $\Delta g(r_{12}; r_i)$ versus $(r_{12}; r_i)$; see Coulson and Neilson (1961) and Boyd and Coulson (1973), respectively. Further comparisons with these lower states were made by evaluating $\langle \phi \rangle_{\text{ip}}$, where $-2 \leq n \leq 2$.

Alternative studies of atomic DES have been made by Berry and co-workers (Rehmus et al 1978, Rehmus and Berry 1979, Ezra and Berry 1983, Krause et al 1987). They invoked comparisons with a trilinear 'floppy molecule' whereby vibrational, rotational and bending quantum numbers could be assigned to each DES. Both Berry and co-workers (see above) and Nicolaides and co-workers (Komninos et al 1986, Nicolaides et al 1987) have examined various conditional probability densities; they used a different approach and a different form of correlated DES wavefunction to that employed here.

2. Wavefunctions and calculations

With the normalized spin function separated from the wavefunction, the explicitly-correlated space function for the $2p^23P$ state was expressed as

$$\Psi_{\text{corr}}(r_1, r_2) = (1 - P_{12}) \sum_{i,j,k}^N A_{ijk} r_1^i r_2^j r_{12}^k \exp(-\alpha_1 - \beta r_2) \tilde{\Omega}^{M=1}_{i,j,k} L=L=1(\theta_1, \phi_1, \theta_2, \phi_2)$$

(1)

where

$$\tilde{\Omega}^{M=1}_{i,j,k} L=L=1(\theta_1, \phi_1, \theta_2, \phi_2) = \frac{1}{\sqrt{2}} [Y^1_1(\theta_1, \phi_1) Y^0_0(\theta_2, \phi_2) - Y^0_0(\theta_1, \phi_1) Y^1_1(\theta_2, \phi_2)]$$

(2)

and $Y^m_l(\theta, \phi)$ is a standard spherical harmonic function. $P_{12}$ is a permutation operator which ensures the antisymmetry of $\Psi_{\text{corr}}(r_1, r_2)$; $A_{ijk}, \alpha$ and $\beta$ are adjustable parameters used in the energy variational method, and the choice of the integers $i, j$ and $k$ is such that $i \geq 1, j \geq 1, k \geq 0$ and $i + j + k \leq N$, where $N$ is a fixed integer governing the size and complexity of the wavefunction. Labels $l_1, l_2$ and $L$ are the azimuthal quantum numbers for electrons 1, 2 and the total system, respectively. $M = 1$ is the total magnetic quantum number.

Of the several wavefunctions provided by one of us (Drake 1986), we examined two for each $Z$: the energetically-best function and, for comparison, the wavefunction with the fewest terms. The summation limit $N$, the total energy $E$ and the percentage of correlation energy recovered by each wavefunction are given in table 1. When $Z \geq 2$, ...
Table 1. Wavefunctions and the N value, the total energy $E$ and the percentage of correlation energy recovered for each $2p^2\,{}^3P$ system. Atomic units are used throughout this work.

<table>
<thead>
<tr>
<th>System</th>
<th>Wavefunction $2p^2,{}^3P$</th>
<th>Energy $-E$ (au)</th>
<th>Percentage of correlation$^a$</th>
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</thead>
<tbody>
<tr>
<td>H$^-$</td>
<td>HF(NUM)</td>
<td>0.115 8840</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>D-20$^b$</td>
<td>0.125 3285</td>
<td>99.72</td>
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<tr>
<td></td>
<td>D-84</td>
<td>0.125 3536</td>
<td>99.99</td>
</tr>
<tr>
<td></td>
<td>'Exact'$^c$</td>
<td>0.125 3547</td>
<td>100.00</td>
</tr>
<tr>
<td>He</td>
<td>HF(NUM)</td>
<td>0.701 4105</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>D-13</td>
<td>0.710 4935</td>
<td>99.93</td>
</tr>
<tr>
<td></td>
<td>D-70</td>
<td>0.710 5001</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>'Exact'$^d$</td>
<td>0.710 5002</td>
<td>100.00</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>HF(NUM)</td>
<td>1.787 269</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>D-13</td>
<td>1.796 640</td>
<td>99.92</td>
</tr>
<tr>
<td></td>
<td>D-70</td>
<td>1.796 648</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>'Exact'$^e$</td>
<td>1.796 648</td>
<td>100.00</td>
</tr>
<tr>
<td>Be$^{2+}$</td>
<td>HF(NUM)</td>
<td>3.373 173</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>D-13</td>
<td>3.382 706</td>
<td>99.93</td>
</tr>
<tr>
<td></td>
<td>D-70</td>
<td>3.382 712</td>
<td>100.00</td>
</tr>
<tr>
<td></td>
<td>'Exact'$^e$</td>
<td>3.382 712</td>
<td>100.00</td>
</tr>
</tbody>
</table>

$^a$ Defined as $[(E_{\text{corr}} - E_{\text{HF}}) / (E_{\text{exact}} - E_{\text{HF}})] \times 100\%$, see Löwdin (1959).

$^b$ D-20, for example, refers to the Drake (1986) wavefunction with $N=20$, this being the value of the summation limit $N$ in equation (1).

$^c$ Taken from Jäuregui and Bunge (1979).

$^d$ Taken from Drake (1986).

$^e$ Taken from Bhatia (1970).

Following Coulson and Neilson (1961), the Coulomb hole $\Delta f(r_{12})$ is defined as the difference between the correlated and HF normalized distributions for the interparticle scalar separation $r_{12} = |r_1 - r_2|$. The partial hole $\Delta g(r_{12}; r_1)$ is similarly defined except that the test electron, particle 1, has a fixed value of $r_1 = |r_1|$; see Boyd and Coulson (1973) and also Banyard and Reed (1981). We note that the integral of $\Delta g(r_{12}; r_1)$ with respect to $r_1$ equals $\Delta f(r_{12})$ which, in turn, integrates to zero. The angular integrations in the formulation of these distribution functions for the $2P$ state are obviously more complex than those for the $1S$ ground state; see, for example, Calais and Löwdin (1962) and Benesch (1972). A schematic orbital representation of the $2p^2\,{}^3P$ state and the coordinate system are shown in figure 1; the origin is centred...
on the nucleus. For discussion purposes, the $f_{HF}(r_{12})$ curves are given in figure 2 for $1 \leq Z \leq 4$; also shown is $f(r_{12})$ generated from an independent-particle $2p^2\,^3P$ wavefunction comprising unoptimized hydrogenic orbitals. In figure 3, the Coulomb holes are displayed for each system and, where appropriate, comparisons are made with the $\Delta f(r_{12})$ curves for $1s2p\,^3P$ and the ground state $1s\,^1S$ (taken, respectively, from Thakkar (1987) and Banyard and Seddon (1973)). The curves for these lower states were also

![Figure 1](image1.png)

**Figure 1.** A schematic orbital representation of the $2p^2\,^3P$ state in position space. Also shown are typical locations of the two electrons in the $2p_0$ and $2p_1$ orbitals.

![Figure 2](image2.png)

**Figure 2.** The $f(r_{12})$ distributions for $H^-$, He, Li$^+$ and Be$^{2+}$ calculated from the $2p^2\,^3P$ Hartree-Fock wavefunctions, $HF$(STO), where $r_{12} = |r_1 - r_2|$. The broken curve is $f(r_{12})$ generated from an independent-particle $2p^2\,^3P$ wavefunction using unoptimized hydrogenic orbitals. Each axis is scaled as shown, thus preserving normalization.
Figure 3. Coulomb holes, $\Delta f(r_{12}) = f_{\text{corr}}(r_{12}) - f_{\text{HF}}(r_{12})$, for (a) $\text{H}^-$, (b) $\text{He}$, (c) $\text{Li}^+$ and (d) $\text{Be}^{++}$. The DES results (full curves) are derived, in turn, from the D-20 and D-84 correlated wavefunctions for $\text{H}^-$, and from the D-13 and D-70 correlated functions for $\text{He}$, $\text{Li}^+$ and $\text{Be}^{++}$. The $1s^2\,^1S$ results (dotted curves) and the $1s^2p\,^3P$ results (broken curves) and taken from Banyard and Seddon (1973) and Thakkar (1987), respectively. The $\Delta f(r_{12})$ scale for $1s^2\,^1S$ is shown on the right of each diagram.
derived from accurate explicitly-correlated wavefunctions and from STO-based HF descriptions. Using the energetically-best correlated functions given in table 1, the DES results for $\Delta f(r_{12})$ are plotted against $Z_{12}$ in figure 4 and, employing the same wavefunctions, the corresponding $g_{HF}(r_{12}; r_1)$ and $\Delta g(r_{12}; r_1)$ distributions are presented as surfaces in figure 5. Contour diagrams of $\Delta g(r_{12}; r_1)$ are shown in figure 6. Table 2 lists $\langle r_{12}^2 \rangle$, the standard deviation $\sigma$ for each $f(r_{12})$ distribution and $\gamma$. The latter quantity is the overall percentage of $f_{HF}(r_{12})$ which has been redistributed due to Coulomb correlation. In passing, table 2 reveals excellent agreement between the HF(NUM) and HF(STO) expectation values.

Atomic units are used throughout figures 2–6 and tables 1 and 2.

3. Discussion

In the independent-particle representation of the $2p^2\,^3P$ state, figure 1 shows one 2p orbital aligned along the $z$-axis and the other located somewhere in the $(x, y)$ plane: the difference between them being solely in their angular parts. Replacement of a 2p function by a 1s orbital creates the singly-excited state $1s2p\,^1P$: the orbitals now differ angularly and radially. For the $^1S$ ground state, besides the obvious change in spin properties, the restricted HF description employs identical 1s orbitals. Thus, it is difficult to anticipate, in any detail, the correlation characteristics of the $2p^2\,^3P$ state from a knowledge of the $1s2p\,^1P$ and $1s\,^1S$ correlation effects (Banyard and Youngman 1982, Thakkar 1987, Curl and Coulson 1965, Banyard and Seddon 1973).

From figure 2 we see that a simple scaling procedure, which also preserves normalization, brings the various $f_{HF}(r_{12})$ curves into some rough correspondence. However, we note that the curve for the weakly bound $H^-$ ion is still relatively diffuse compared with those for the bound systems He, Li$^+$ and Be$^{2+}$. As $Z$ increases, the curves approach the broken curve derived from the unoptimized hydrogenic radial functions. This arises because the electron-electron repulsion term becomes an ever-decreasing perturbation, compared with the electron-nuclear attraction potential, as $Z \to \infty$. The presence of Fermi correlation in the description of the $^3P$ state produces, as expected, a flat region which is effectively zero near the origin of each $f_{HF}$-curve.

3.1. Coulomb holes

Inspection of the Coulomb holes for the $2p^2\,^3P$ states in figure 3 shows that the $r_{12}$
The doubly-excited state $2p^2^3P$ for $1 \leq Z \leq 4$

range for H\(^-\) is at least six times that for He, whereas the comparison between the ranges for He and Be\(^{2+}\) is only about 2:1. The diffuseness of the correlation effect is so large for H\(^-\) that the HF and the correlated $f(r_{12})$ distributions are qualitatively different: a feature not apparent when $Z \geq 2$. This is highlighted by relating the $r_{12}$ range for a given $\Delta f(r_{12})$ with that for the corresponding $f_{HF}(r_{12})$ function plotted in figure 2. For example, we note that the $r_{12}$ value which encompasses 98% of $f_{HF}(r_{12})$ is 27.6 for H\(^-\) and 9.0, 5.5 and 3.9 for He, Li\(^+\) and Be\(^{2+}\), respectively. With the exception of H\(^-\), each DES curve in figure 3 shows that the magnitude of $\Delta f(r_{12})$ beyond the relevant $r_{12}$ value is small, thus indicating that the effects of correlation are essentially located in the major regions of $f_{HF}(r_{12})$. This observation is clearly not valid when $Z = 1$. The dramatic change caused by correlation for H\(^-\) is also reflected in the value for Y in table 2: the very large result of 27.9% is to be compared with 5.64% for He, 3.63%(Li\(^+\)) and 2.69%(Be\(^{2+}\)).

Table 2. Expectation values $\langle r_{12}^2 \rangle$, where $r_{12} = |r_1 - r_2|$, for the states $2p^3^3P$, $1s2p^3^3P$ and $1s^2^1S$. Also shown is $\sigma$, the standard deviation, and Y, the percentage of $f_{HF}(r_{12})$ which has been redistributed due to electron correlation.

<table>
<thead>
<tr>
<th>System</th>
<th>Wavefunction</th>
<th>$\langle r_{12}^2 \rangle$</th>
<th>$\langle r_{12}^4 \rangle$</th>
<th>$\langle r_{12} \rangle$</th>
<th>$\langle r_{12}^2 \rangle$</th>
<th>$\sigma$</th>
<th>Y (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^-) ($2p^3^3P$)</td>
<td>HF(NUM)</td>
<td>0.013 956</td>
<td>0.102 84</td>
<td>12.277</td>
<td>184.97</td>
<td>5.851 9</td>
<td>—</td>
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<tr>
<td></td>
<td>HF(STO)</td>
<td>0.013 953</td>
<td>0.102 83</td>
<td>12.281</td>
<td>185.06</td>
<td>5.851 7</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>D-20(^a)</td>
<td>0.006 8550</td>
<td>0.072 425</td>
<td>17.922</td>
<td>413.87</td>
<td>9.627 1</td>
<td>26.50</td>
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<td>0.070 630</td>
<td>19.237</td>
<td>517.09</td>
<td>12.125 6</td>
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<td></td>
<td>(1s^2^1S)</td>
<td>HF(^b)</td>
<td>0.289 32</td>
<td>0.394 44</td>
<td>3.772 2</td>
<td>19.394</td>
<td>2.272 5</td>
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<td>corr</td>
<td>0.157 53</td>
<td>0.313 50</td>
<td>4.377 3</td>
<td>24.870</td>
<td>2.398 8</td>
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<tr>
<td>He ($2p^3^3P$)</td>
<td>HF(NUM)</td>
<td>0.090 997</td>
<td>0.268 79</td>
<td>4.474 7</td>
<td>23.381</td>
<td>1.832 4</td>
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<td>0.268 79</td>
<td>4.474 7</td>
<td>23.382</td>
<td>1.832 5</td>
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<td>0.077 283</td>
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<td>4.675 7</td>
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<td>0.266 12</td>
<td>4.744 2</td>
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<td>Li(^+) ($2p^3^3P$)</td>
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<td>2.758 7</td>
<td>8.833 1</td>
<td>1.105 8</td>
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<td>HF(STO)</td>
<td>0.234 62</td>
<td>0.433 13</td>
<td>2.758 7</td>
<td>8.833 1</td>
<td>1.105 8</td>
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<tr>
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<td>D-70</td>
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<td>0.415 00</td>
<td>2.838 6</td>
<td>9.245 3</td>
<td>1.089 9</td>
<td>3.63</td>
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<tr>
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<td>(1s2p^3^3P)</td>
<td>HF(^c)</td>
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<td>HF(NUM)</td>
<td>0.444 89</td>
<td>0.597 31</td>
<td>1.995 1</td>
<td>4.609 1</td>
<td>0.792 75</td>
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<tr>
<td></td>
<td>HF(STO)</td>
<td>0.444 89</td>
<td>0.597 31</td>
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<td>4.609 1</td>
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<tr>
<td></td>
<td></td>
<td>corr</td>
<td>8.038 4</td>
<td>2.191 8</td>
<td>0.618 55</td>
<td>0.477 67</td>
<td>0.308 33</td>
</tr>
</tbody>
</table>

\(^a\) D-20, for example, refers to the Drake (1986) wavefunction with $N = 20$ in the summation limit in equation (1).

\(^b\) For $1s^2^1S$, the STO-based HF and explicitly-correlated results are taken from Banyard and Seddon (1973).

\(^c\) For $1s2p^3^3P$, the STO-based HF and explicitly-correlated results were calculated by Thakkar (1987).
Figure 5. Partial Coulomb hole densities \( \Delta g(\rho_2; r_1) - \Delta g_{\text{HF}}(\rho_2; r_1) \), for (a) \(^1\text{H}^+\), (b) \(^3\text{He}^+\), (c) \(^7\text{Li}^+\) and (d) \(^9\text{Be}^{7+}\) in the \( 2p^2 3P \) state, where \( r_2 = |\mathbf{r}_2 - \mathbf{r}_1| \) and \( n = |n|\).

The \( \Delta g_{\text{HF}}(\rho_2; r_1) \) distributions and the \( \Delta g(\rho_2; r_1) \) surfaces are obtained from the energetically-best correlated wavefunctions and the HF(STR) representations, respectively.

Note the changes in scales for the \( \Delta g \) and \( \Delta g_{\text{HF}} \) surfaces as \( Z \) is increased.
The doubly-excited state $2p^2 \ ^3P$ for $1 \leq Z \leq 4$

Figure 5. (continued)
The Fermi effect causes each $^3P$ Coulomb hole to be effectively zero at small $r_{12}$—unlike the behaviour of the $^1S$ holes (we note that, being larger, the $\Delta f(r_{12})$ values for the ground state have their own scale on the right of each diagram). Nevertheless, the DES curves in figure 3 are of the same general shape as the $^1S$ holes although, naturally, they are much more diffuse. For $Z \geq 2$, the $1s2p\,^3P$ holes possess an $r_{12}$ range comparable with the DES curves but are of different shape due to the noticeable subsidiary minimum in the outer region. The origin of the $1s2p\,^3P$ outer minimum has been discussed in detail by Banyard and Youngman (1982) and by Thakkar (1987). The radius of the Coulomb hole, being the first non-zero value of $r_{12}$ when $\Delta f(r_{12}) = 0$, shows a not surprising increase, relative to the ground state, as first one and then the second electron is described by a p orbital (coupled, of course, with a change in the overall spin description). For each DES curve except for $H^-$, the crossover point or node has an $r_{12}$ value which is approximately equal to that at the peak of the appropriate $f_{HF}(r_{12})$ distribution. In addition, as seen from figure 4, these nodes can be brought into relatively reasonable coincidence by using a $Zr_{12}$ scale. Such a finding parallels that observed for the ground state by Curl and Coulson (1965) and for the $1s2p\,^3P$ state by Thakkar (1987). Furthermore, following Curl and Coulson, the degree of coincidence could be improved by plotting $\Delta F(r_{12})$ against $(Z-k)r_{12}$. Excluding the $Z = 1$ result, a screening parameter of $k = 0.39$ brought the remaining DES nodes into
excellent agreement at 6.20 ± 0.05. Interestingly, the ground-state improvement required a $k$ value of 0.38.

When $Z \geq 2$, figure 3 indicates that, on the present scale, the Coulomb holes cannot be used to differentiate between the D-13 and D-70 wavefunctions. Such a conclusion is not too unexpected since, as shown in table 1, the correlation percentages are large and almost identical. However, for $H^-$, where the D-20 and D-84 functions differ in their correlation percentages by 0.27%, the $\Delta f(r_{12})$ curves are easily distinguishable with the larger and energetically better function producing the slightly deeper and more diffuse hole. These observations are supported by the values of $\langle r_{12}^p \rangle$ and $\sigma$ in table 2. Although the energy improvement is small for $H^-$, $\sigma$ and $\langle r_{12} \rangle$ are much larger for D-84 than for D-20 whereas, for the electron-electron repulsion term $\langle r_{12}^1 \rangle$, a noticeable decrease occurs. Similar trends exist for $Z \geq 2$ but, as seen from table 2, each change is greatly reduced in magnitude.

To assess any Hylleraas-type wavefunction by inspection is not easy. The introduction of more terms usually adds higher powers of $r_1$, $r_2$, and $r_{12}$ and hence improves both radial and angular correlation, the latter being directly dependent on the $r_{12}$-terms. Nevertheless, with reference to equation (1), a brief comment on the exponential parameters $\alpha$ and $\beta$ is worthwhile. Very crudely, these parameters dictate the general form of the two-particle radial distribution. For He and the positive ions, it was found that $\alpha$ and $\beta$ differ by 30% at most, with the relative difference decreasing with increasing $Z$. But for $H^-$, $\alpha$ is at least three times $\beta$ for both the 20- and 84-term wavefunctions. This suggests that, like the ground state, the diffuseness of the Coulomb hole for $H^-$ in figure 4 arises from a massive ‘in-out’ effect in the radial component of electron correlation. As $Z$ gets larger, the reduced relative difference between $\alpha$ and $\beta$ indicates the decreasing importance of such an effect.

### 3.2. Partial Coulomb holes

In figure 5 we note the changes in scale as we progress from $H^-$ to $Be^{2+}$ and, in addition, we recall that the integrated volume under each $g_{HF}(r_{12}; r_1)$ surface is unity whereas for $\Delta g(r_{12}; r_1)$ is zero. Naturally, the Fermi effect produces a flat region at small $r_{12}$ for all $r_1$ values.

Inspection of the data for each $g_{HF}(r_{12}; r_1)$ revealed that its maximum was located at a point where $r_{12} > r_1$ and that the surface as a whole was biased towards the $r_{12} > r_1$ side of the $r_{12} = r_1$ diagonal. This corresponds to the orbital model in figure 1. Moreover, the coordinates of the maximum were found to be in rough accord with the theorem of Pythagoras. The $\Delta g(r_{12}; r_1)$ diagrams in figures 5 and 6 show that, as the test electron 1 is moved away from the nucleus, the partial Coulomb hole continues to encompass the nucleus within its sphere of influence. Eventually, however, the radius of the partial hole (i.e. the $r_{12}$ value such that $\Delta g = 0$) becomes less than the fixed $r_1$ value. The increase in radius with the increase in $r_1$ could be related to the reduced momentum of electron 1 as it moves away from the nucleus. This would enhance the ability of the other electron to avoid the test electron, so producing a more extensive ‘hole’.

For $H^-$, the $\Delta g(r_{12}; r_1)$ surface in figure 5 shows that the effect of correlation spreads noticeably beyond the $(r_{12}; r_1)$ range used for $g_{HF}(r_{12}; r_1)$. This is clearly not the case when comparing the $\Delta g$ and $g_{HF}$ surfaces for $Z \geq 2$. Such a contrasting feature supports our earlier observations regarding the relative diffuseness of the $H^-$ distribution. The $\Delta g(r_{12}; r_1)$ surface for $H^-$ is also distinctive since it possesses well defined characteristics parallel to the $r_{12}$-axis and along the $r_{12} = r_1$ diagonal. This is admirably
illustrated by the contour diagrams in figure 6. To interpret these characteristics, we assume that the test electron is located at fixed distances \( r \), along, say, the \( z \)-axis of the \( 2p \) orbital and that the 'roving' electron is described by the \( 2p \) orbital; see figure 1. When \( r \) is small, the proximity of the test electron to the nucleus produces a shielding effect in excess of that provided by the HF potential. Thus, the \( 2p \) orbital responds to electron correlation by becoming more diffuse. The probability density is therefore reduced at small \( r > \) and increased for large \( r < \).

For \( \text{H}^- \), the one-particle radial distribution for the HF representation of the \( 2p \) state was found to be a maximum at \( r = 5 \). Hence, electron correlation ought to produce its greatest reduction when \( r \) and \( r < \) are each \( -5 \). Therefore, from Pythagoras, the minimum in \( \Delta g(r_{12}; r) \) for \( \text{H}^- \) should occur when \( r \approx 5 \) and \( r < 7 \). This is confirmed in figure 6(a). The above rationale accounts for the 'parallel' characteristics.

When \( r \) is large, the influence of the distant test electron on the 'roving' electron is significantly less than that produced by the HF potential centred on the nucleus. Consequently, relative to the HF description, the \( 2p \) orbital is contracted towards the nucleus. To locate the 'roving' electron in the vicinity of the nucleus when \( r \) is sizeable obviously requires a comparable value for \( r_{12} \). Thus, for any large fixed \( r \), we anticipate that electron correlation will increase the probability density when \( r_{12} = r \). For \( \text{H}^- \), the \( \Delta g \) contours show that, for the example of \( r = 20 \), a positive effect extends across the range \( 16 < r_{12} < 26 \). That the increase is not symmetric about the \( r_{12} = r \) diagonal-point arises from there being more of the \( 2p \) orbital located in the \( r_{12} > r \) region than in the \( r_{12} < r \) region. However, when the fixed \( r \) value is increased, the spherical surface of radius \( r_{12} = r \) (centred at the test electron on the \( z \)-axis) will then divide the \( 2p \) orbital into more nearly equal upper and lower portions; see figure 1. Hence, the positive region across the diagonal should become larger and, in particular, the asymmetry of the effect will be reduced. As seen from figure 6(a), the 'diagonal' feature for \( \text{H}^- \) has therefore been established.

Additional information can be obtained from \( \Delta g(r_{12}; r) \) by integrating over \( 0 \leq r_{12} \leq \infty \) to yield \( \Delta D(r) \), the change in the one-particle radial distribution due to correlation. For \( \text{H}^- \), the well defined characteristics in figure 6(a) indicate that \( \Delta D(r) \) would reveal an extensive split-shell behaviour. This confirms the massive 'in-out' influence of radial correlation discussed earlier. When \( Z > 1 \), the two-, three- and four-fold increase in nuclear attraction shifts the 'parallel' and 'diagonal' patterns in \( \Delta g(r_{12}; r) \) towards the origin, thus allowing them to overlap and merge. Even so, the more simplified contour diagrams for \( \text{He}, \text{Li}^+ \) and \( \text{Be}^{2+} \) displayed in figure 6 still retain features indicative of the behaviour seen for \( \text{H}^- \). Naturally, they become slightly less obvious as \( Z \) increases.

Disregarding the differences in the coordinate range, the \( \Delta g \) characteristics for \( Z = 2 \) and 3 show marked similarities to those for the He and Li\(^+\) ground states, respectively (see figures 2(\( j \)) and 2(\( d \)) of Banyard and Reed (1981)). For \( Z = 3 \) again and \( Z = 4 \), a corresponding similarity occurs when comparisons are made with the \( K\alpha K\beta \) characteristics in the Li and Be\(^+\) ground states (Al-Bayati (1984) and, for Li\(^{(2)S}\), see figures 5 and 6 of Banyard and Al-Bayati (1986)). Comparisons between these \( \Delta g \) surfaces obviously discount the Fermi effect at small \( r_{12} \).

3.3. Expectation values

Being totally integrated quantities, the values for \( \langle r_{12}^n \rangle \) are less informative than the Coulomb holes regarding the consequences of electron correlation. Nevertheless, table
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2 does show that correlation reduces the DES and ground-state results for $n \leq -1$ and increases them when $n \geq +1$. This also occurs for the $1s2p^3P$ state when $Z \geq 3$. In absolute terms, $\langle r_{12}^n \rangle$ emphasizes, quite reasonably, a similarity between $2p^2 3^P$ and $1s2p^3P$, rather than with the $1S$ ground state. This is reinforced by inspection of the first two moments $\langle r_{12} \rangle$ and $\sigma$. For Li$^+$ and Be$^{2+}$, Table 2 also indicates that both these values for $2p^2 3^P$ are in excess of those for $1s2p^3P$ whereas, for He, the reverse is the case.

4. Summary

The analysis of correlation effects in the doubly-excited state $2p^2 3^P$ for $1 \leq Z \leq 4$ was performed in terms of the Coulomb holes, $\Delta f(r_{12})$ versus $r_{12}$, derived from the use of explicitly-correlated wavefunctions. These wavefunctions, being of high accuracy, recovered well in excess of 99% of the correlation energy.

Comparisons with the $1s^2 1S$ ground state and with the singly-excited state $1s2p^3P$ revealed that the DES systems possessed correlation characteristics similar in behaviour, but not in scale, to those for the ground state. The Coulomb holes for $2p^2 3^P$ and $1s2p^3P$, although of comparable range, exhibited different characteristics. Consequently, the common features of electron correlation observed here are dictated by the apparent ‘doubly occupancy’ of the states, irrespective of differences caused by spin properties. The range of the effect for a given $Z$ is obviously governed by the spatial extent of the orbitals.

For each DES system, the influence of correlation was noticeably greater than that found for the ground state. This can be highlighted by comparing the values for $Y$: the overall change caused by correlation in the normalized distribution function for $r_{12}$. For Be$^{2+}$, for example, $Y$ for the $2p^2 3^P$ state is about 22% larger than the ground-state value whereas, for the weakly-bound H$^-$ ion, the increase on the ground-state value is almost 250%. The distinction between the negative ion and the other systems was also emphasized by the partial Coulomb holes, $\Delta g(r_{12}; r_1)$ versus $(r_{12}; r_1)$. The significant diffuseness observed for H$^-$ enabled us to identify and rationalize two basic correlation characteristics which, since they partially overlap when $Z > 1$, were more difficult to resolve as $Z$ increased. Such features should be applicable to any ‘double-occupancy’ state.

Finally, an analysis of the separate angular and radial components of electron correlation has now been completed for these $2p^2 3^P$ states. The probability distribution for the interelectronic angle, various angular and radial expectation values and several statistical correlation coefficients will be reported shortly. The results may be compared with a ‘molecular’ interpretation of a DES atom as a floppy trilinear molecule; see Ezra and Berry (1983) and references therein.

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