Expectation values of $p_1 \cdot p_2$ as a measure of electron correlation in two-electron atoms

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We examine expectation values of $p_1 \cdot p_2$ in ground states of He and H−, the singly and doubly excited states of He, and the ground and low-lying valence states of the alkaline-earth-metal atoms. A simple commutator relation derived by Froese Fischer and Smentek-Mielczarek [J. Phys. B 16, 3479 (1983)] can be used to explain the sign and relative magnitudes of $\langle p_1 \cdot p_2 \rangle$ in the ground states of He and H− and singly excited states of He. In the doubly excited states of He and in the ground and low-lying valence states of the alkaline-earth metals, the molecular model, which treats the electron—core-electron system as a floppy, linear triatomic “molecule,” correctly predicts signs and general trends for $\langle p_1 \cdot p_2 \rangle$. These results represent an important test of the molecular model. The ability of this model to make intuitive predictions about quantities like $\langle p_1 \cdot p_2 \rangle$ is a strong confirmation of its validity and utility.

INTRODUCTION

It is now well known that electron correlation in the doubly excited states of helium and the ground and low-lying states of the alkaline-earth-metal atoms and alkali-metal negative ions is so important that it can dominate the dynamics of the valence electrons. Several models have been developed to treat this strong correlation. In the hyperspherical method, the correlation is studied in the coordinates $R \equiv (r_1^2 + r_2^2)^{1/2}$ and $a \equiv \tan^{-1}(r_2/r_1)$. Lin1 has used this method, for example, to assign angular correlation quantum numbers $K$ and $T$ which were introduced by Sinanoğlu and Herrick2 and radial correlation quantum number $A$ to the doubly excited states of two-electron atoms. Lin,3 O’Mahony,4 and Greene5 have also used the hyperspherical method to study electron correlation in the alkaline-earth atoms. The model that we will concentrate on in this paper treats the electron—core-electron system as a floppy, linear “triatomic molecule.” This model was initially suggested by Herrick and Kellman6 as a way of explaining the pattern of energy levels in doubly excited helium. Later work has shown that conditional probability distributions for doubly excited helium,7 the alkaline-earth atoms8 and alkali-metal negative ions9 exhibit the characteristics expected for their assignment in the molecular model. It has also recently been shown that the hyperspherical method can be used to examine the molecular nature of these systems.10,11

Until now, tests of the molecular model have been largely qualitative. That is, the model predicts that the conditional probability distributions for a given state have certain qualitative features or that its position in an energy-level diagram12 corresponds to a particular assignment of quantum numbers. However, the molecular model also has some definite quantitative implications. We report here the results of an exploration of one probe of the degree of molecular correlation in two-electron atoms. We examine expectation values of the inner product of the linear momenta $\langle p_1 \cdot p_2 \rangle$ for the ground, singly, and doubly excited states of helium and the ground and low-lying excited states of the alkaline-earth metals. The signs and relative magnitudes of $\langle p_1 \cdot p_2 \rangle$ confirm the assignments of these states in the molecular model. Such an independent, quantitative test of the model is important not only as a way of checking the validity of the model itself, but in making predictions for experiments.

In the graphical analysis of the helium doubly excited states and of the alkaline-earth atoms and alkali-metal negative ions, conditional probability distributions $\rho(r_1, \theta_{12} | r_1 = \xi)$ are constructed in configuration space to examine the degree of molecular character in a given state.7–9 These distributions display the probabilities of finding one electron at a distance $r_2$ from the nucleus with angle $\theta_{12}$ between the two $r$ vectors, given that the other electron is fixed at a distance $\xi$ from the nucleus. Since $\cos \theta_{12} = r_1 \cdot r_2 / (r_1 r_2)$, a natural quantity to examine in momentum space which is related to the configuration-space quantity $\rho$ is $p_1 \cdot p_2$. Further, as we shall see, in the strongly correlated molecular states expectation values of $p_1 \cdot p_2$ make some especially simple predictions.

Some simple commutator algebra can be used to show...
how \( p_1 \cdot p_2 \) is related to \( r_1 \cdot r_2 \) and hence to \( \theta_{12} \). Consider
\[
\langle [H, r_1 \cdot p_2 + p_1 \cdot r_2] \rangle_{\psi} = \langle [r_1 \cdot p_2 + p_1 \cdot r_2, V] \rangle_{\psi}.
\]
where \( \psi \) is a bound-state eigenfunction of the Hamiltonian and
\( H = T + V \), where \( T \) and \( V \) are the kinetic energy and the potential energy, respectively. Since this quantity vanishes,
\[
\langle [T, r_1 \cdot p_2 + p_1 \cdot r_2] \rangle_{\psi} = \langle [p_1^2 r_2, p_1] \rangle_{\psi} + \frac{1}{2} \langle [p_1^2 r_2, p_1] \rangle_{\psi} = -i \langle p_1 \cdot p_2 + p_1 \cdot p_1 \rangle_{\psi}.
\]
Similarly,
\[
\langle [r_1 \cdot p_2 + p_1 \cdot r_2, V] \rangle_{\psi} = -i \langle r_1 \cdot \nabla V + r_2 \cdot \nabla V \rangle_{\psi}.
\]
Thus,
\[
2 \langle p_1 \cdot p_2 \rangle_{\psi} = \langle r_1 \cdot \nabla V + r_2 \cdot \nabla V \rangle_{\psi}.
\]
This relation, which is analogous to the virial theorem
\[
\langle p_1^2 + p_2^2 \rangle_{\psi} = -\langle r_1 \cdot \nabla V + r_2 \cdot \nabla V \rangle_{\psi},
\]
holds for any bound state of the Hamiltonian. It cannot be expected to hold for scattering or resonant states. If
\[
V = -\frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}
\]
then
\[
\nabla V = Z \frac{r_2}{r_1} - \frac{r_2 - r_1}{r_{12}}
\]
and
\[
\nabla V = Z \frac{r_1}{r_2} - \frac{r_1 - r_2}{r_{12}}.
\]
By substituting Eqs. (3) and (4) into (1), we obtain the relation previously presented by Froese Fischer and Smentek-Mielczarek.\(^{13}\)
\[
2 \langle p_1 \cdot p_2 \rangle_{\psi} = \langle Z \frac{r_1}{r_1} + \frac{r_2}{r_2} \rangle_{\psi}.
\]
Equation (5) holds for a bound eigenfunction of a helium-like ion. [It will not hold for quasi-two-electron systems, where the electron-nucleus Coulomb potentials in (2) are replaced by non-Coulombic pseudopotentials.] We can now use this relation to predict the sign and magnitude of \( \langle p_1 \cdot p_2 \rangle \) for the ground and singly excited states of helium.

### HELIUM AND H\(^-\) GROUND STATES

The nominal configuration of the \( 1^1S \) ground state of helium is \((1s)^2\). If there were no electron correlation (e.g., if one turned off the \( 1/r_{12} \) term, or replaced it with an average value as in the spherical approximation to Hartree-Fock theory), then \( \langle p_1 \cdot p_2 \rangle \) for this state would be 0. In the "real" helium-atom ground state, \( \langle p_1 \cdot p_2 \rangle \) is positive\(^{14}\) (see Table I). This can be rationalized from the

<table>
<thead>
<tr>
<th>( N )</th>
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<th>( N )</th>
<th>( 1^3S )</th>
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<td>1</td>
<td>(He^-)</td>
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<tr>
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<td>2</td>
<td>0.2238920</td>
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<tr>
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<td>-0.00389</td>
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<td>-0.00216</td>
<td>12</td>
<td>0.00059</td>
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Table I. Values of \( \epsilon_n = (1/M) \langle p_1 \cdot p_2 \rangle \) in \( \text{cm}^{-1} \), where \( M \) is the nuclear mass, for the ground and several singly-excited states of helium and the ground state of H\(^-\). The value for the ground state of H\(^-\) is from Pekeris (Ref. 15) and the rest are from Kono and Hattori (Ref. 14). Note that \( M \) for H\(^-\) is different from that for He.

Commutator relations. In helium the \( 1^1S \) state exhibits relatively little angular correlation [see Fig. 1(a)]; thus the positive and negative contributions to
\[
\langle r_1 \cdot r_2 \left[ \frac{1}{r_1} + \frac{1}{r_2} \right] \rangle_{\psi}
\]
tend to cancel each other. On the other hand, the contributions to \( \langle 1/r_{12} \rangle \) all are positive, so the net effect is to make \( \langle p_1 \cdot p_2 \rangle \) positive. The same analysis holds for the \( 1^3S \) state of H\(^-\).\(^{15}\) Although this state is more correlated than the ground state of helium, most of the correlation is radial, and so \( \langle p_1 \cdot p_2 \rangle \) is still positive. Table I also shows that \( \langle p_1 \cdot p_2 \rangle \) is, in fact, smaller by a factor of 5 for the ground state of H\(^-\) than for the ground state of helium. This is because the electrons in H\(^-\) are considerably more diffuse radially than in He [see Fig. 1(f)].

### HELIUM SINGLY EXCITED STATES

Singly excited states of two-electron atoms and positive ions are described well, in lowest order, within an independent-particle model, where the spatial dependence of the wave function is a symmetrized sum of products of single-particle functions:
\[
\psi_\pm = \frac{1}{\sqrt{2}} \left[ 1s(11n(2)) \pm n(1)1s(2) \right],
\]
where + corresponds to a singlet state and - to a triplet. If we calculate \( \langle p_1 \cdot p_2 \rangle \) in the state \( \psi_\pm \), we find that
\[
\langle p_1 \cdot p_2 \rangle_{\psi_\pm} = \pm \langle 1s \mid p \mid n \rangle^2.
\]
Furthermore, by angular momentum selection rules,
FIG. 1. Conditional probability distributions \( p(r_z, \theta_{12} \mid r_1 = \xi) \) for (a) the ground state of He, (b) the He 2s \(^2\)S\(^e\), (c) the He 2p \(^2\)D\(^e\), (d) the He 2s 2p \(^1\)P\(^e\), (e) the He 2s 3s \(^1\)S\(^e\), and (f) the ground state of H\(^-\). The nucleus is located at the center of each plot, and the position of the fixed electron is denoted by a small sphere. The fixed electron is located at its most probable position in each case. The maximum value of \( r \) is 5.0 bohr, and \( \theta_{12} = 0 \) is denoted by a vertical bar.

\[
\langle 1s \mid p \mid nl \rangle \text{ vanishes unless } l = 1, \text{ which corresponds to a total } L \text{ of 1. Thus we see that if } \psi_+ \text{ does not have a total } L \text{ of 1, } \langle p_1 \cdot p_2 \rangle \text{ should be rather small, with magnitude coming only from the relatively small correlation effects, and if } \psi_+ \text{ has } L = 1, \text{ then } \langle p_1 \cdot p_2 \rangle \text{ will be rather different from 0, and}
\]

\[
\langle p_1 \cdot p_2 \rangle_{\psi_+} = -\langle p_1 \cdot p_2 \rangle_{\psi_-}.
\]

We may test these qualitative predictions against the highly accurate calculations by Kono and Hattori\(^{14}\) of \( \epsilon_m = \langle 1/M \rangle \langle p_1 \cdot p_2 \rangle \), where \( M \) is the nuclear mass in atomic units, for a number of \( S, P, \) and \( D \) states of helium (see Table I). We see from Table I that our expectations are confirmed: The values of \( \langle p_1 \cdot p_2 \rangle \) for the \( N_{1S}^1P \) states of helium are at least four times larger than the corresponding values for the \( N_{1S}^1S \) states. Further, for the \( S \) states,

\[
\langle p_1 \cdot p_2 \rangle_{\psi_+} \simeq \langle p_1 \cdot p_2 \rangle_{\psi_-},
\]

but that for the \( P \) states,

\[
\langle p_1 \cdot p_2 \rangle_{\pm} \simeq -\langle p_1 \cdot p_2 \rangle_{\phi_+},
\]

thus confirming our predictions based on the uncorrelated zeroth-order singly excited wave functions. It can also be noted that the magnitude of \( \langle p_1 \cdot p_2 \rangle \) decreases with increasing Rydberg character. This is because as we move from a state with nominal configuration \( 1s^2 \) to one with a configuration \( 1s5s \), the two electrons begin to occupy rather different regions of space. As a result, \( \langle 1/r_{12} \rangle \) and hence \( \langle p_1 \cdot p_2 \rangle \) becomes rather small. The high-lying Rydberg states are also almost pure configuration states, for which \( \langle p_1 \cdot p_2 \rangle = 0 \).

Finally, as expected from the above analysis, the values of \( \langle 1/M \rangle \langle p_1 \cdot p_2 \rangle \) for the \( ^1D \) states, with nominal configuration \( 1sn \), are all quite small.

HELIUM DOUBLY EXCITED STATES
AND LOW-LYING STATES
OF THE ALKALINE-EARTH METALS

Since the doubly excited states of helium are resonances and not true bound states, Eq. (1) cannot be used to analyze \( \langle p_1 \cdot p_2 \rangle \). We could find no published values for \( \langle p_1 \cdot p_2 \rangle \) for these states, so we developed a program to calculate them. To do this, we first constructed Sturmian variational wave functions for the state of interest, details of which have been published previously.\(^7\) Table II shows that our calculated energies for these states agree well with those obtained from the high-quality, complex-scaling calculations of Hoo.\(^6\) We found that because the expectation values of \( p_1 \cdot p_2 \) are very small, obtaining good convergence of the wave functions was important. It was also important to include basis functions of high angular momentum and so these calculations include functions with \( l \leq 6 \). Having obtained the wave functions, we evaluated \( \langle p_1 \cdot p_2 \rangle \) using formulas derived from relations found in Bethe and Salpeter.\(^7\) The formulas used for these calculations are found in the Appendix.

Previous work has shown that the molecular model successfully describes many aspects of the electron correlation in doubly excited helium.\(^6,7\) Figures 1(b), 1(c), 1(d), and 1(e), for example, show conditional probability distributions \( p(r_z, \theta_{12} \mid r_1 = \xi) \) for some of these states in a polar representation. It can be seen, for example, that the helium \( 2p^2 \ ^1D^e \) state, which is given the assignment of 2
TABLE II. Comparison of energies calculated with Sturmian variational wave functions (this work) with complex-scaling calculations of Ho (Ref. 16). All energies are in rydbergs.

<table>
<thead>
<tr>
<th>State</th>
<th>Term</th>
<th>$-E$ (Sturmian)</th>
<th>$-E$ (Ho)</th>
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<tr>
<td>$2s^2$</td>
<td>$^1S_e$</td>
<td>1.555 73</td>
<td>1.555 74</td>
</tr>
<tr>
<td>$2s 2p$</td>
<td>$^3P_o$</td>
<td>1.520 99</td>
<td>1.521 00</td>
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<td>$2p^2$</td>
<td>$^1D_e$</td>
<td>1.405 99</td>
<td>1.405 63</td>
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<tr>
<td>$2s 2p$</td>
<td>$^1P_o$</td>
<td>1.386 26</td>
<td>1.386 27</td>
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<td>$^3P_e$</td>
<td>1.420 86</td>
<td>1.421 00</td>
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<td>1.243 86</td>
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<tr>
<td>$2s 3s$</td>
<td>$^3S_e$</td>
<td>1.179 92</td>
<td>1.179 85</td>
</tr>
</tbody>
</table>

The highly correlated $2s^2$ state and the virtually uncorrelated $1s^2$ ground state of helium is striking. The $2s 2p$ $^1P_o$ state is given the assignment of one quantum of bending excitation, and the distribution has the correct qualitative shape for a bending vibration. The distribution has two lobes, corresponding to the two classical turning points, at about $\theta_{12} = \pm 135^\circ$. Finally, the $2s 3s$ $^1S_e$ state is a state with one quantum of symmetric stretching excitation, and the distribution shows two radial lobes, one toward and the other away from the nucleus from the fixed electron.

This molecular model makes some definite "zeroth-order" predictions for the expectation values of $p_1 \cdot p_2$ in these states. For example, in the rotor states, since the electrons are moving in "opposite" directions, the sign of $\langle p_1 \cdot p_2 \rangle$ should be negative whereas in the bending states, since the two electrons are moving in the "same" direction, the sign of $\langle p_1 \cdot p_2 \rangle$ should be positive. These predictions are summarized in Fig. 2. Our results for $\langle p_1 \cdot p_2 \rangle$ for the doubly excited states of helium are shown in Table III. Since

$$-T = -\frac{1}{2} (p_1^2 + p_2^2) \leq \langle p_1 \cdot p_2 \rangle \leq \frac{1}{2} (p_1^2 + p_2^2) = T$$

FIG. 2. Predictions of the signs of $\langle p_1 \cdot p_2 \rangle$ in doubly excited helium based on a classical description of the motion of the electrons for a given assignment in the molecular model.
TABLE III. Calculated values of $\langle p_1^2 p_2^2 \rangle / \langle T \rangle$ for helium doubly excited states. Numbers in square brackets are powers of ten.

<table>
<thead>
<tr>
<th>State</th>
<th>Term</th>
<th>$\langle p_1^2 p_2^2 \rangle / \langle T \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2s^2$</td>
<td>$1S^e$</td>
<td>$-1.01[-3]$</td>
</tr>
<tr>
<td>$2s 2p$</td>
<td>$1P^o$</td>
<td>$-1.45[-3]$</td>
</tr>
<tr>
<td>$2p^2$</td>
<td>$1D^e$</td>
<td>$-0.71[-3]$</td>
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<td>$2s 2p$</td>
<td>$1P^o$</td>
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</tr>
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</tr>
<tr>
<td>$2s 3s$</td>
<td>$3S^e$</td>
<td>$1.45[-2]$</td>
</tr>
</tbody>
</table>

we have tabulated

$$\frac{\langle p_1^2 p_2^2 \rangle}{\langle T \rangle} \quad (13)$$

as a reasonable normalized quantity, where $\langle T \rangle$ is the kinetic energy. A comparison of Fig. 2 and Table III shows that the sign of $\langle p_1^2 p_2^2 \rangle$ is predicted correctly by the molecular model for every state. It can also be seen that the magnitude of $\langle p_1^2 p_2^2 \rangle$ for the $2s^2$ ground state is very small, and that the magnitude of $\langle p_1^2 p_2^2 \rangle$ increases both with increasing rotational and vibrational excitation, as expected.

The procedure for the ground and low-lying states of the alkaline-earth atoms is very similar to that of the helium doubly excited states. We treat the alkaline-earth-metal atoms as quasi-two-electron atoms by using pseudopotentials, in this case, as reported previously, those of Bachelet, Hamann, and Schlüter. Because of the pseudopotential approximation, we cannot use Eq. (5) and must calculate $\langle p_1^2 p_2^2 \rangle$. The results of these calculations for magnesium are shown in Table IV. Results for the other alkaline-earth-metal atoms are similar, though the agreement with the model becomes somewhat worse as the atom gets heavier. This may be partially because the calculations of the wave functions for the heavier atoms are not as good, but may also be because as the atom becomes heavier, the “molecule” becomes flippier. This means that we may be seeing a mixture of angular and radial correlation effects. Table IV shows that the molecular model again predicts the general trends in $\langle p_1^2 p_2^2 \rangle$. There are a few discrepancies, however. The value of $\langle p_1^2 p_2^2 \rangle$ for the Mg ground state is somewhat large compared to the rest of the rotor states. This is possibly a result of radial correlation, which, were the state a pure rotor, would be absent. The sign of the $3s 4s 1S^e$ state is also incorrectly predicted. This is quite possibly due to the fact that, as discussed previously, the stretch states of the alkaline-earth atoms go rather quickly to independent-particle behavior as the position of the fixed electron moves either toward or away from the nucleus. The singlet state, in particular, has a fair amount of Rydberg character, and is really a state which is described well by neither the independent particle model nor the molecular model.

CONCLUSIONS

We have shown that the expectation value of $p_1^2 p_2^2$, in the ground states of He and H− in the singly excited states of He can be understood on the basis of some straightforward commutator algebra. In the doubly excited states of He and the ground- and low-lying states of the alkaline-earth metals, however, it is the molecular model which presents the natural, intuitive explanation. The ability of the model to make simple and valid predictions based on a classical notion of the dynamics of the electrons in these states is an important confirmation of its applicability.

This work is, however, only a first step in the effort to quantify the molecular model. We had hoped that $\langle p_1^2 p_2^2 \rangle$ could be used as a quantitative test to assign a state unambiguously in the molecular model. This would be especially useful in the heavier atoms such as bariun, where “interloper states” and the crossing of energy levels make the assignment of states in the molecular model problematical. In fact, we find that while the sign of $\langle p_1^2 p_2^2 \rangle$ and the relative magnitude of $\langle p_1^2 p_2^2 \rangle$ within a rotor series, for example, is important, it is not obvious how the absolute magnitude of $\langle p_1^2 p_2^2 \rangle$ can be used to assign a state in the model. One reason for this difficulty is that $\langle p_1^2 p_2^2 \rangle$ contains both radial and angular correlation. Work is in progress to look at expectation values of other operators which might distinguish these two contributions. This might also clarify the analysis of the alkaline-earth metals, for which the model molecule is rather floppy, and some states have mixtures of molecular and independent-particle character. We are also investigating the possibility of computing wave functions and expectation values in momentum space, which might well be a more natural way to proceed. Regier and Thakkar have recently demonstrated that this is a very feasible approach. The graphical analysis in momentum space might also lead to some interesting insights.

Our interpretation of the expectation values of $p_1^2 p_2^2$ may also help to illuminate some of the previous, and ongoing, discussion of the importance of such operators in a variety of areas of atomic physics. For instance, the dipole oscillator strength distribution $df/dE$ is central to the understanding of such phenomena photoionization and inelastic collisions of fast charged particles with atoms and molecules. A number of the moments of this distribution

TABLE IV. Calculated values of $\langle p_1^2 p_2^2 \rangle / \langle T \rangle$ for the ground and low-lying states of magnesium.

<table>
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<td>$3P^e$</td>
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<td>$3s 4s$</td>
<td>$1S^e$</td>
<td>$3.57[-2]$</td>
</tr>
<tr>
<td>$3s 4s$</td>
<td>$3S^e$</td>
<td>$5.98[-2]$</td>
</tr>
</tbody>
</table>
\[ S(\mu) = \int \frac{E}{R} \left[ \frac{df}{dE} \right]^\mu dE, \]  

(14)

where \( R \) is the Rydberg energy, obey optical sum rules which depend on the ground-state properties of an atom. The first moment of the distribution, \( S(1) \), is related to expectation values of \( p_i \cdot p_j \) by \(^{22}\)

\[ S(1) = \frac{4}{3R} \left[ \sum_j \frac{p_j^2}{2m} + \sum_k \sum_{k \neq j} \frac{p_j \cdot p_k}{2m} \right], \]  

(15)

where \( m \) is the mass of the electron. Similarly, the minus first moment of the distribution is related to expectation values of \( r_i \cdot r_j \) by \(^{22}\)

\[ S(-1) = \left( 3a_0^2 \right)^{-1} \sum_j \langle r_j^2 \rangle + \sum_k \sum_{k \neq j} \langle r_j \cdot r_k \rangle, \]  

(16)

where \( a_0 \) is the Bohr radius. A number of authors have remarked that these two moments, in particular, are related to the \( \theta_{12} \) dependence, and thus the angular correlation, of the electrons in a given atom. \(^{22-25}\)

Another area of recent experimental and theoretical interest in which the conclusions of this paper may be of relevance is the isotope shift of atomic spectral lines. This quantity is a standard correction term in atomic calculations \(^{26}\) and has also recently been shown to be important in the determination of interstellar isotope abundances. \(^{27}\) The isotope shift operator, which is a consequence of the finiteness of the nuclear mass, can be decomposed as \(^{27}\)

\[ \frac{p_i^2}{2M} = \frac{1}{2M} \sum_i p_i^2 + \frac{1}{2M} \sum_{i,j \neq i} p_i \cdot p_j, \]  

(17)

where \( M \) is the nuclear mass. Experimental determination of the expectation value of the first part of this operator, the so-called normal isotope shifts, is fairly straightforward, but the second part, the specific mass shift, presents considerable difficulty. Fassett and coworkers \(^{28,29}\) are currently measuring the isotope shift in the alkaline-earth-metal atoms with at least one motivation being the study of electron correlation in these atoms. Since experimental determination of the specific mass term is difficult, our calculations may aid in the understanding of the factors which contribute to the composition of this term. They are not directly applicable, however, since we have calculated \( \langle p_1 \cdot p_2 \rangle \) for the valence electrons with a model potential and have not yet determined the contributions of the core electrons. Nonetheless, an interaction between theory and experiment may well lead to an understanding of some of the factors which influence the isotope shift and thus some of the effects of electron correlation in these atoms.

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**APPENDIX**

To calculate \( \langle p_1 \cdot p_2 \rangle \) we begin with Eqs. (A37)–(A39) of Bethe and Salpeter. \(^{16}\) If \( f \) is any function of the radial distance \( r \) alone,

\[ \frac{\partial}{\partial x} \left[ f(r) \right] Y_{lm} (\theta, \varphi) = \left( \frac{l + m + 1}{2l + 3} \right) Y_{l+1,m} \left( \frac{df}{dr} - \frac{l f}{r} \right), \]  

(A37)

Similarly,

\[ \frac{\partial}{\partial x} \left[ f Y_{lm} \right] = \left( \frac{l + m + 2}{2l + 3} \right) Y_{l+1,m+1} \left( \frac{df}{dr} - \frac{l f}{r} \right), \]  

(A38)

\[ \frac{\partial}{\partial y} \left[ f Y_{lm} \right] = \left( \frac{l - m - 1}{2l + 1} \right) Y_{l-1,m+1} \left( \frac{df}{dr} + \frac{(l + 1) F}{r} \right), \]  

(A39)

Since \( \langle p_1 \cdot p_2 \rangle \) is invariant under rotation, we can take \( M \) to be 0. Then, the total wave function can be written as

\[ \psi = \sqrt{2L+1} \sum_{l_1,l_2} \sum_{m} Y_{l_1,m-} | \theta_{l_1,\varphi_{l_1}} Y_{l_1,m-} (\theta_2, \varphi_2) \rangle, \]

where, in our case,
\[ f_{l_1,l_2}(r_1,r_2) = \sum_{n_1,n_2} c_{n_1,l_1,n_2,l_2} \phi_{n_1,l_1}(r_1) \phi_{n_2,l_2}(r_2) \]

and

\[ \phi(r) = \mathcal{N} r^{m-\varepsilon}. \]

\( \mathcal{A} \) is the antisymmetrizing operator and \( \mathcal{N} \) is the normalization constant. After extensive algebra and integration over the four angles, we find that

\[
\langle \mathbf{p}_1 \cdot \mathbf{p}_2 \rangle = \sum_{l_1,l_2,m} \int dr_1 r_1^2 \int dr_2 r_2^2 \frac{\partial f_{l_1+1,l_2+1}}{\partial r_1} + (l_1 + 2) \frac{f_{l_1+1,l_2+1}}{r_1} \left[ \begin{array}{c} l_1 + 1 \\ m \\ \end{array} \right] \left[ \begin{array}{c} f_{l_1,l_2} \\ L \\ \end{array} \right] \left[ \begin{array}{c} l_1 \\ l_2 \\ L \\ \end{array} \right] \left( \frac{l_1 - m + 1}{2l_1 + 1} \right) \left( \frac{l_1 + m + 1}{2l_1 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right) \left( \frac{l_2 + m + 1}{2l_2 + 1} \right) \left( \frac{l_1 + m + 2}{2l_1 + 1} \right) \left( \frac{l_1 + m + 2}{2l_1 + 1} \right)
\]

\[
	imes \left[ \begin{array}{c} l_1 + 1 \\ m + 1 \\ \end{array} \right] \left[ \begin{array}{c} l_2 + 1 \\ L \\ \end{array} \right] \left[ \begin{array}{c} l_1 + m + 2 \\ l_1 + m + 1 \\ \end{array} \right] \left( \frac{l_1 + m + 2}{2l_1 + 1} \right) \left( \frac{l_1 + m + 1}{2l_1 + 1} \right) \left( \frac{l_2 + m + 2}{2l_2 + 1} \right) \left( \frac{l_2 + m + 1}{2l_2 + 1} \right) \left( \frac{l_2 + m + 2}{2l_2 + 1} \right) \left( \frac{l_2 + m + 1}{2l_2 + 1} \right)
\]

\[
+ \sum_{l_1,l_2,m} \int dr_1 r_1^2 \int dr_2 r_2^2 \frac{f_{l_1+1,l_2+1}}{r_1} \left[ \begin{array}{c} l_1 + 1 \\ m + 1 \\ \end{array} \right] \left[ \begin{array}{c} l_2 + 1 \\ L \\ \end{array} \right] \left[ \begin{array}{c} l_1 + m + 2 \\ l_1 + m + 1 \\ \end{array} \right] \left( \frac{l_1 + m + 2}{2l_1 + 1} \right) \left( \frac{l_1 + m + 1}{2l_1 + 1} \right) \left( \frac{l_2 + m + 2}{2l_2 + 1} \right) \left( \frac{l_2 + m + 1}{2l_2 + 1} \right) \left( \frac{l_2 + m + 2}{2l_2 + 1} \right) \left( \frac{l_2 + m + 1}{2l_2 + 1} \right)
\]

\[
+ \sum_{l_1,l_2,m} \int dr_1 r_1^2 \int dr_2 r_2^2 \frac{f_{l_1+1,l_2+1}}{r_1} \left[ \begin{array}{c} l_1 - 1 \\ m - 1 \\ \end{array} \right] \left[ \begin{array}{c} l_2 - 1 \\ L \\ \end{array} \right] \left[ \begin{array}{c} l_1 - m + 2 \\ l_1 - m + 1 \\ \end{array} \right] \left( \frac{l_1 - m + 2}{2l_1 + 1} \right) \left( \frac{l_1 - m + 1}{2l_1 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right)
\]

\[
+ \sum_{l_1,l_2,m} \int dr_1 r_1^2 \int dr_2 r_2^2 \frac{f_{l_1+1,l_2+1}}{r_1} \left[ \begin{array}{c} l_1 - 1 \\ m - 1 \\ \end{array} \right] \left[ \begin{array}{c} l_2 - 1 \\ L \\ \end{array} \right] \left[ \begin{array}{c} l_1 - m + 2 \\ l_1 - m + 1 \\ \end{array} \right] \left( \frac{l_1 - m + 2}{2l_1 + 1} \right) \left( \frac{l_1 - m + 1}{2l_1 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right)
\]

\[
+ \sum_{l_1,l_2,m} \int dr_1 r_1^2 \int dr_2 r_2^2 \frac{f_{l_1+1,l_2+1}}{r_1} \left[ \begin{array}{c} l_1 - 1 \\ m - 1 \\ \end{array} \right] \left[ \begin{array}{c} l_2 - 1 \\ L \\ \end{array} \right] \left[ \begin{array}{c} l_1 - m + 2 \\ l_1 - m + 1 \\ \end{array} \right] \left( \frac{l_1 - m + 2}{2l_1 + 1} \right) \left( \frac{l_1 - m + 1}{2l_1 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right)
\]

\[
+ \sum_{l_1,l_2,m} \int dr_1 r_1^2 \int dr_2 r_2^2 \frac{f_{l_1+1,l_2+1}}{r_1} \left[ \begin{array}{c} l_1 - 1 \\ m - 1 \\ \end{array} \right] \left[ \begin{array}{c} l_2 - 1 \\ L \\ \end{array} \right] \left[ \begin{array}{c} l_1 - m + 2 \\ l_1 - m + 1 \\ \end{array} \right] \left( \frac{l_1 - m + 2}{2l_1 + 1} \right) \left( \frac{l_1 - m + 1}{2l_1 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right) \left( \frac{l_2 - m + 2}{2l_2 + 1} \right) \left( \frac{l_2 - m + 1}{2l_2 + 1} \right)
\]
\[
+ \sum_{l_1, l_2, m} \int dr_1 r_1^2 \int dr_2 r_2^2 \left[ \frac{\partial f_{l_1-1, l_2-1}}{\partial r_1} \left( l_1 - 1 \right) \frac{f_{l_1-1, l_2-1}}{r_1} \right] \\
\times \left[ \frac{\partial f_{l_1, l_2}}{\partial r_2} + (l_2 + 1) \frac{f_{l_1, l_2}}{r_2} \right] \\
\times \begin{vmatrix} l_1 & l_2 & L \\ m & -m & 0 \end{vmatrix} \left[ \frac{(l_1 - m)(l_1 + m)}{(2l_1 + 1)(2l_1 - 1)} \right]^{1/2} \left[ \frac{(l_2 - m)(l_2 + m)}{(2l_2 + 1)(2l_2 - 1)} \right]^{1/2} \\
- \frac{1}{2} \begin{vmatrix} l_1 & l_2 & L \\ m + 1 & -m - 1 & 0 \end{vmatrix} \left[ \frac{(l_1 - m)(l_1 + m - 1)}{(2l_1 + 1)(2l_1 - 1)} \right]^{1/2} \left[ \frac{(l_2 - m)(l_2 - m - 1)}{(2l_2 + 1)(2l_2 - 1)} \right]^{1/2} \\
- \frac{1}{2} \begin{vmatrix} l_1 & l_2 & L \\ m - 1 & -m + 1 & 0 \end{vmatrix} \left[ \frac{(l_1 + m)(l_1 + m - 1)}{(2l_1 + 1)(2l_1 - 1)} \right]^{1/2} \left[ \frac{(l_2 + m)(l_2 + m - 1)}{(2l_2 + 1)(2l_2 - 1)} \right]^{1/2}
\]

Note that the above formula does not depend on a specific choice of \( f_{l_1, l_2}(r_1, r_2) \).