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# Statistical electron correlation coefficients for the five lowest states of the heliumlike ions

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Statistical correlation coefficients were introduced by Kutzelnigg, Del Re, and Berthier to provide overall measures of the difference between the electron pair density and the product of one-electron densities in atoms and molecules. Some properties of these coefficients are discussed, and it is shown that an angular correlation coefficient is experimentally accessible. Radial and angular correlation coefficients are computed from highly accurate wave functions for the $1\,^1S$, $2\,^3S$, $2\,^1S$, $2\,^3P$, and $2\,^1P$ states of the heliumlike ions from He through $Mg^{10+}$. It is found that positive angular correlation coefficients occur in the $2\,^1P$ state of the two-electron positive ions but not in neutral helium. Moreover, the angular correlation coefficients for the $2\,^1S$ and $2\,^3S$ states of the positively charged two-electron ions show that a previously proposed reformulation of Hund's rule is incorrect.

## I. INTRODUCTION

The term electron correlation is commonly used in two different senses. In the conventional quantum-chemistry sense electron correlation effects are those that are not taken into account by the Hartree-Fock approximation.[1] In the statistical sense electron correlation is the manner in which the electron pair density differs from the product of the one-electron densities.[2] The electron pair density[3] for an $n$-electron system in a state characterized by the wave function $\psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n)$ is defined by

$$D_2(\vec{r}_1, \vec{r}_2) = \int \psi^*(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n) \times \psi(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_n)\, d\sigma_1 d\sigma_2 d\vec{x}_3 d\vec{x}_4 \ldots d\vec{x}_n\,,$$

where $\vec{x}_i = (\vec{r}_i, \sigma_i)$ is a combined space-spin coordinate and the one-electron density[3] is the following contraction of the two-electron density:

$$D_1(\vec{r}_1) = \int D_2(\vec{r}_1, \vec{r}_2) d\vec{r}_2 = \int D_2(\vec{r}_2, \vec{r}_1) d\vec{r}_2\,.$$

The statistical correlation between the electrons is described by the statistical pair correlation density defined by

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

The two meanings of electron correlation are not equivalent because the antisymmetry of the Hartree-Fock wave function accounts for the Fermi correlation[4] between electrons of like spin. Thus the Hartree-Fock wave function leads to a nonvanishing pair correlation density $c(\vec{r}_1, \vec{r}_2)$ for systems with two or more electrons of like spin.[5] The terms electron correlation and pair correlation density will be used in the statistical sense throughout this paper.

It is difficult to visualize the correlation density because it is a rather complicated function of six variables.[6] Hence it is useful to have numerical indices which provide overall measures of the correlation density. Such indices were introduced by Kutzelnigg, Del Re, and Berthier[7] who used concepts from probability theory and mathematical statistics to define generalized correlation coefficients $\tau_g$ for functions $g(\vec{r})$ of the electronic position vectors. They[7] define

$$\tau_g = \frac{\left(\frac{2n}{n-1}\right) \langle \sum_{i>j} g(\vec{r}_i) g(\vec{r}_j) \rangle - \langle \sum_i g(\vec{r}_i) \rangle^2}{n \langle \sum_i g^2(\vec{r}_i) \rangle - \langle \sum_i g(\vec{r}_i) \rangle^2}\,. \qquad (1)$$

Expectation values of local one- and two-electron operators can be expressed in terms of the one- and two-electron densities in the following manner:

$$\left\langle \sum_{i>j} h(\vec{r}_i, \vec{r}_j) \right\rangle = \frac{n(n-1)}{2} \int D_2(\vec{r}_1, \vec{r}_2) h(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2\,,$$

$$\left\langle \sum_i g(\vec{r}_i) \right\rangle = n \int D_1(\vec{r}_1) g(\vec{r}_1) d\vec{r}_1\,.$$

Moreover, the densities have been normalized to unity:

$$\int D_2(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = \int D_1(\vec{r}_1) d\vec{r}_1 = 1\,.$$

Therefore the correlation coefficient $\tau_g$ may be rewritten as

$$\tau_g = \frac{\int c(\vec{r}_1, \vec{r}_2) g(\vec{r}_1) g(\vec{r}_2) d\vec{r}_1 d\vec{r}_2}{\int D_1(\vec{r}_1) D_1(\vec{r}_2) g(\vec{r}_1) [g(\vec{r}_1) - g(\vec{r}_2)] d\vec{r}_1 d\vec{r}_2}\,.$$

Evidently $\tau_g$ vanishes for statistically uncorrelated pair densities. Note that the denominator of the above expression can be rewritten in a symmetrized form so that

$$\tau_g=\frac{\int c(\vec{r}_1,\vec{r}_2)g(\vec{r}_1)g(\vec{r}_2)d\vec{r}_1d\vec{r}_2}{\frac{1}{2}\int D_1(\vec{r}_1)D_1(\vec{r}_2)[g^2(\vec{r}_1)+g^2(\vec{r}_2)-2g(\vec{r}_1)g(\vec{r}_2)]d\vec{r}_1d\vec{r}_2}. \tag{2}$$

## II. RADIAL CORRELATION COEFFICIENTS

Radial correlation coefficients may be defined by the requirement that the function $g(\vec{r})$ in the definitions (1) and (2) be spherically symmetric; that is, $g(\vec{r})=R(r)$ where $r=|\vec{r}|$. Radial correlation coefficients $\tau_R$ depend only on the radial part of the two-electron density

$$\bar{D}_2(r_1,r_2)=r_1^2r_2^2\int D_2(\vec{r}_1,\vec{r}_2)d\Omega_1d\Omega_2 .$$

The radial one-electron density can be obtained by the single integration

$$\bar{D}_1(r_1)=r_1^2\int D_1(\vec{r}_1)d\Omega_1$$

$$=\int_0^\infty \bar{D}_2(r_1,r_2)dr_2=\int_0^\infty \bar{D}_2(r_2,r_1)dr_2 ,$$

and the radial pair correlation density is

$$\bar{c}(r_1,r_2)=r_1^2r_2^2\int c(\vec{r}_1,\vec{r}_2)d\Omega_1d\Omega_2$$

$$=\bar{D}_2(r_1,r_2)-\bar{D}_1(r_1)\bar{D}_1(r_2) .$$

Thus

$$\tau_R=\frac{\int_0^\infty\int_0^\infty \bar{c}(r_1,r_2)R(r_1)R(r_2)dr_1dr_2}{\frac{1}{2}\int_0^\infty\int_0^\infty \bar{D}_1(r_1)\bar{D}_1(r_2)[R^2(r_1)+R^2(r_2)-2R(r_1)R(r_2)]dr_1dr_2} .$$

The simple choice $R(r)=r^k$ yields the radial correlation coefficients

$$\tau_{r^k}=\frac{\left(\frac{2n}{n-1}\right)\langle\sum_{i>j}r_i^kr_j^k\rangle-\langle\sum_i r_i^k\rangle^2}{n\langle\sum_i r_i^{2k}\rangle-\langle\sum_i r_i^k\rangle^2} .$$

The coefficients $\tau_{r^k}$ depend on the choice of the origin. The nucleus is the natural origin for atoms, whereas molecules generally do not have a natural origin. The coefficients corresponding to the specific choices $k=+1$ and $k=-1$ were introduced by Kutzelnigg and co-workers,[7] and have been studied for the ground states of the berylliumlike ions by Banyard and Mashat.[8]

## III. ANGULAR CORRELATION COEFFICIENTS IN ATOMS

Kutzelnigg and his colleagues[7] used the function $g(\vec{r})=\vec{r}$ to define an angular correlation coefficient for atoms. Choosing the nucleus as the origin, and interpreting the product of vectors in (1) and (2) as a scalar product they obtained[9]

$$\tau_{\vec{r}}=\frac{2\langle\sum_{i>j}\vec{r}_i\cdot\vec{r}_j\rangle}{(n-1)\langle\sum_i r_i^2\rangle}$$

$$=\frac{2\langle\sum_{i>j}r_ir_j\cos\theta_{ij}\rangle}{(n-1)\langle\sum_i r_i^2\rangle} ,$$

where $\theta_{ij}$ is the angle subtended at the nucleus by the electronic position vectors $\vec{r}_i$ and $\vec{r}_j$. A natural generalization is provided by the choice of the function $g(\vec{r})=\vec{r}/r^k$. The specific case $k=0$ leads to the angular coefficient given above, and the case $k=1$ leads to the particularly simple angular correlation coefficient

$$\tau_{\vec{r}/r}=\frac{2}{n(n-1)}\left\langle\sum_{i>j}(\vec{r}_i/r_i)\cdot(\vec{r}_j/r_j)\right\rangle$$

$$=\frac{2}{n(n-1)}\left\langle\sum_{i>j}\cos\theta_{ij}\right\rangle .$$

These angular correlation coefficients are bounded in absolute value by unity:

$$-1\leq\tau_{\vec{r}}\leq+1 ,$$

$$-1\leq\tau_{\vec{r}/r}\leq+1 .$$

Perfect positive correlation ($\tau=+1$) means that the position vectors of a pair of electrons are expected to coincide whereas perfect negative correlation ($\tau=-1$) implies that electron pairs are expected to be at diametrical positions with respect to the nucleus. If the angular correlation coefficient is zero then the electrons are either independent $[c(\vec{r}_1,\vec{r}_2)=0]$ or merely uncorrelated by virtue of orthogonality of their position vectors.

It is of some interest to note that the ground-state angular correlation coefficient $\tau_{\vec{r}}$ is related to the oscillator strength distribution by virtue of the sum rule[10]

$$S(-1)=\sum_k E_{0k}^{-1}f_{0k}=\tfrac{2}{3}\left\langle\sum_{i,j}\vec{r}_i\cdot\vec{r}_j\right\rangle ,$$

where $f_{0k}$ is the spherically averaged dipole oscillator strength for the transition from the ground state to the $k$th state, $E_{0k}$ is the corresponding transition energy, and the expectation value is with respect to the ground state. Thus

$$S(-1)=\tfrac{2}{3}\left\langle\sum_i r_i^2\right\rangle[1+(n-1)\tau_{\vec{r}}\,].$$

Since $\langle\sum_i r_i^2\rangle$ can be obtained from the diamagnetic susceptibility and $S(-1)$ from the oscillator strength distribution, the angular correlation coefficient $\tau_{\vec{r}}$ for the ground state can, in principle, be obtained from experimental measurements exclusively.

For atoms in $S$ states, $D_2(\vec{r}_1,\vec{r}_2)$ is invariant[11] under simultaneous and equal rotations of $\vec{r}_1$ and $\vec{r}_2$. Therefore one may write

$$D_2(\vec{r}_1,\vec{r}_2)=\sum_{L=0}^{\infty}D_2^L(r_1,r_2)P_L(\cos\theta_{12}),$$

where $P_L(x)$ is a Legendre polynomial. The one-electron density for an $S$-state atom is spherically symmetric,

$$D_1(\vec{r}_1)=D_1(r_1)=4\pi\int_0^\infty r_2^2D_2^0(r_1,r_2)dr_2,$$

and, as Bingel[12] has pointed out, the angular correlation coefficient $\tau_{\vec{r}}$ depends only on the $L=0$ and 1 components of the Legendre expansion of the pair density. In fact,

$$\tau_{\vec{r}}=\frac{\frac{1}{3}\int_0^\infty\int_0^\infty r_1^3r_2^3D_2^1(r_1,r_2)dr_1dr_2}{\frac{1}{2}\int_0^\infty\int_0^\infty r_1^2r_2^2(r_1^2+r_2^2)D_2^0(r_1,r_2)dr_1dr_2}.$$

Similarly the angular coefficient $\tau_{\vec{r}/r}$ for $S$ states of an atom depends only on the $L=1$ component of the pair density and is given by

$$\tau_{\vec{r}/r}=\frac{16\pi^2}{3}\int_0^\infty\int_0^\infty r_1^2r_2^2D_2^1(r_1,r_2)dr_1dr_2.$$

## IV. $Z^{-1}$ EXPANSIONS FOR ISOELECTRONIC SERIES

The $Z^{-1}$ perturbation-theory expansion of these correlation coefficients for a given state in an isoelectronic series is of the form

$$\tau_g=a_{g,0}+a_{g,1}Z^{-1}+a_{g,2}Z^{-2}+\dots,$$

provided that $g(\vec{r})$ is a homogeneous function as is the case with all the $g(\vec{r})$ considered in this work. Note that positive powers of the nuclear charge $Z$ do not appear in the expansion unlike the case of the $Z^{-1}$ expansion of the energy. Moreover the symmetry properties of some states may ensure that the constant term $a_{g,0}$ vanishes. For example, $a_{r,0}$, $a_{\vec{r},0}$, and $a_{\vec{r}/r,0}$ all vanish for the ground state of the two-electron atoms. The perturbation-theory results of Midtdal and Aashamar[13] may be used to show that for the ground state of the heliumlike ions,

$$\tau_{\vec{r}}=-0.126\,205\,6Z^{-1}+0.023\,816\,6Z^{-2}+0.016\,942\,0Z^{-3}+O(Z^{-4}).$$

## V. LOW-LYING STATES OF THE HELIUMLIKE IONS

The radial correlation coefficients $\tau_r$ and the angular correlation coefficients $\tau_{\vec{r}}$ and $\tau_{\vec{r}/r}$ were computed for the $1\,^1S$, $2\,^3S$, $2\,^1S$, $2\,^3P$, and $2\,^1P$ states of the heliumlike ions. A systematic collection of highly accurate wave functions[14] that depend explicitly on the interelectronic coordinate was used for the calculations. These wave functions[14] are of the form

$$\psi(\vec{x}_1,\vec{x}_2)=(2L+1)^{1/2}(4\pi)^{-1}2^{-1/2}\times[\alpha(\sigma_1)\beta(\sigma_2)\mp\beta(\sigma_1)\alpha(\sigma_2)]\times\sum_k c_k(1\pm P_{12})r_1^LP_L(\cos\theta_1)\times\exp(-\alpha_kr_1-\beta_kr_2-\gamma_kr_{12}),$$

where $L=0$ and 1 for $S$ and $P$ states, respectively, the upper and lower signs correspond to the sing-

TABLE I. $\tau_r$ for the five lowest states of the heliumlike ions.

| $Z$ | $1\,^1S$ | $2\,^3S$ | $2\,^1S$ | $2\,^3P$ | $2\,^1P$ |
|---|---|---|---|---|---|
| 1 | −0.293 936 | | | | |
| 2 | −0.111 688 | −0.660 198 | −0.678 868 | −0.609 023 | −0.640 228 |
| 3 | −0.068 652 | −0.654 737 | −0.648 655 | −0.577 046 | −0.605 839 |
| 4 | −0.049 609 | −0.650 872 | −0.629 899 | −0.561 626 | −0.585 669 |
| 5 | −0.038 843 | −0.648 334 | −0.618 084 | −0.552 457 | −0.573 046 |
| 6 | −0.031 926 | −0.646 558 | −0.609 554 | −0.546 292 | −0.564 181 |
| 7 | −0.027 102 | −0.645 259 | −0.603 404 | −0.541 921 | −0.557 691 |
| 8 | −0.023 546 | −0.644 268 | −0.598 556 | −0.538 645 | −0.552 713 |
| 9 | −0.020 813 | −0.643 479 | −0.594 751 | −0.536 099 | −0.548 849 |
| 10 | −0.018 648 | −0.642 854 | −0.591 711 | −0.534 089 | −0.545 661 |
| 11 | −0.016 895 | −0.642 332 | −0.589 320 | −0.532 388 | −0.543 044 |
| 12 | −0.015 446 | −0.641 900 | −0.587 122 | −0.531 012 | −0.540 820 |
| ∞ | 0 | −0.636 995 | −0.563 005 | −0.515 789 | −0.515 789 |

TABLE II. $\tau_{\vec{r}}$ for the five lowest states of the heliumlike ions.

| $Z$ | $1\,^1S$ | $2\,^3S$ | $2\,^1S$ | $2\,^3P$ | $2\,^1P$ |
|---|---|---|---|---|---|
| 1 | −0.057 692 | | | | |
| 2 | −0.054 242 | −0.005 127 | −0.003 853 | −0.008 299 | −0.002 134 |
| 3 | −0.038 659 | −0.004 837 | −0.004 991 | −0.016 709 | 0.001 116 |
| 4 | −0.029 757 | −0.004 137 | −0.005 058 | −0.021 257 | 0.005 491 |
| 5 | −0.024 137 | −0.003 550 | −0.004 728 | −0.023 943 | 0.009 072 |
| 6 | −0.020 287 | −0.003 089 | −0.004 367 | −0.025 694 | 0.012 035 |
| 7 | −0.017 491 | −0.002 727 | −0.004 032 | −0.026 918 | 0.014 421 |
| 8 | −0.015 369 | −0.002 438 | −0.003 697 | −0.027 819 | 0.016 353 |
| 9 | −0.013 704 | −0.002 199 | −0.003 441 | −0.028 509 | 0.017 956 |
| 10 | −0.012 364 | −0.002 006 | −0.003 199 | −0.029 057 | 0.019 280 |
| 11 | −0.011 262 | −0.001 840 | −0.002 991 | −0.029 493 | 0.020 418 |
| 12 | −0.010 341 | −0.001 703 | −0.002 775 | −0.029 859 | 0.021 379 |
| ∞ | 0 | 0 | 0 | −0.033 632 | 0.033 632 |

let and triplet states, respectively, $P_{12}$ is a permutation operator that interchanges $\vec{r}_1$ and $\vec{r}_2$, and $\alpha(\sigma)$ and $\beta(\sigma)$ are the usual one-electron spin functions. These wave functions are extremely accurate and their energy errors range from $2\times10^{-9}$ hartrees for the $2\,^3S$ state of He to $5\times10^{-5}$ hartrees for the $2\,^1S$ state of $\mathrm{Ne}^{8+}$. They also predict very accurate values for a wide variety of expectation values,[14] cusp ratios,[14] and zero-momentum energies.[15] The ground-state wave functions have already been used in several applications.[16]

The correlation coefficients are listed in Tables I–III and shown graphically in Figs. 1–3. The values for the infinite nuclear-charge limit were computed exactly and correspond to the constant terms in the $Z^{-1}$ expansions discussed in Sec. IV. In order to join the ground-state He($Z=2$) and $\mathrm{H}^-$($Z=1$) values of $\tau_{\vec{r}}$ in Fig. 2, $\tau_{\vec{r}}$ values at intermediate nonphysical values of $Z$ were computed from ratios of [10/10] Padé approximants[17] to the 20th order $Z^{-1}$ perturbation-theory expansions[13] for $\langle\vec{r}_1\cdot\vec{r}_2\rangle$ and $\langle r_1^2\rangle$. These Padé approximant values are accurate to six and three significant figures for He and $\mathrm{H}^-$, respectively. The radial correlation coefficients in all the excited states and the angular correlation coefficients in the $P$ states are nonzero even in the infinite nuclear-charge limit because of the symmetry properties of the excited-state hydrogenic wave functions. In the ground state the hydrogenic wave function leads to a statistically uncorrelated pair density and hence all the $1\,^1S$ correlation coefficients vanish in the infinite nuclear-charge limit.

The figures clearly show that the ground-state radial correlation between the electrons increases in importance as $Z$ decreases. Moreover the ratio $\tau_r/\tau_{\vec{r}/r}$ increases from 1.4 in $\mathrm{Mg}^{10+}$($Z=12$) to 2.8 in $\mathrm{H}^-$($Z=1$) confirming the well-known fact[18] that radial correlation increases in importance relative to angular correlation as the nuclear charge is decreased. The ground-state angular correlation

TABLE III. $\tau_{\vec{r}/r}$ for the five lowest states of the heliumlike ions.

| $Z$ | $1\,^1S$ | $2\,^3S$ | $2\,^1S$ | $2\,^3P$ | $2\,^1P$ |
|---|---|---|---|---|---|
| 1 | −0.105 148 | | | | |
| 2 | −0.064 203 | −0.015 839 | −0.014 659 | −0.036 714 | −0.004 769 |
| 3 | −0.043 632 | −0.012 645 | −0.014 637 | −0.054 612 | 0.010 370 |
| 4 | −0.032 941 | −0.010 154 | −0.013 136 | −0.062 103 | 0.023 036 |
| 5 | −0.026 437 | −0.008 422 | −0.011 598 | −0.066 054 | 0.031 876 |
| 6 | −0.022 072 | −0.007 177 | −0.010 295 | −0.068 479 | 0.038 498 |
| 7 | −0.018 942 | −0.006 246 | −0.009 234 | −0.070 098 | 0.043 512 |
| 8 | −0.016 588 | −0.005 526 | −0.008 334 | −0.071 254 | 0.047 423 |
| 9 | −0.014 754 | −0.004 953 | −0.007 604 | −0.072 120 | 0.050 549 |
| 10 | −0.013 285 | −0.004 487 | −0.006 981 | −0.072 792 | 0.053 109 |
| 11 | −0.012 081 | −0.004 100 | −0.006 450 | −0.073 329 | 0.055 230 |
| 12 | −0.011 077 | −0.003 775 | −0.005 981 | −0.073 766 | 0.057 025 |
| ∞ | 0 | 0 | 0 | −0.078 037 | 0.078 037 |

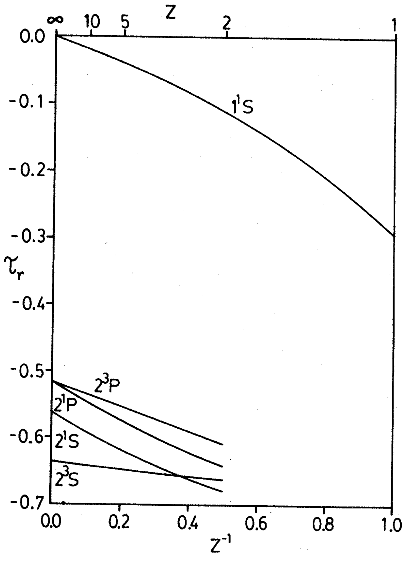

FIG. 1. Radial correlation coefficients.

coefficient $\tau_{\bar{r}}$ appears to have a minimum value of $-0.06962$ around $Z^{-1} \simeq 0.815$ ($Z \simeq 1.227$). Such a minimum must exist because the two-electron atom becomes unbound for low enough nuclear charge[19] and hence the angular correlation coefficients must vanish for low enough $Z$.

The differences between singlet and triplet states arising from the same configuration have recently been discussed by very many authors[20] in connection with the interpretation of Hund's rule. The presence of the Fermi hole in the triplet leads to differences in the correlation coefficients for the singlet and triplet even in the infinite-$Z$ limit. This is clearly shown by $\tau_r$ for the $S$ states, and by the angular correlation coefficients for the $P$ states.

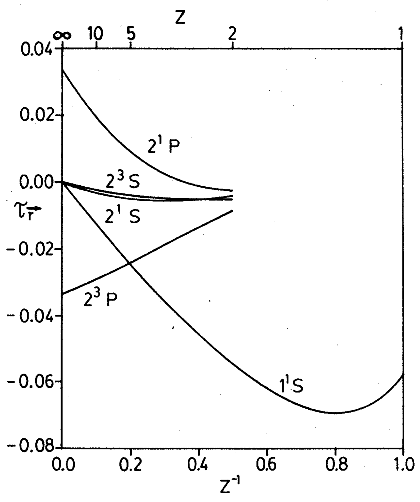

FIG. 2. Angular correlation coefficients.

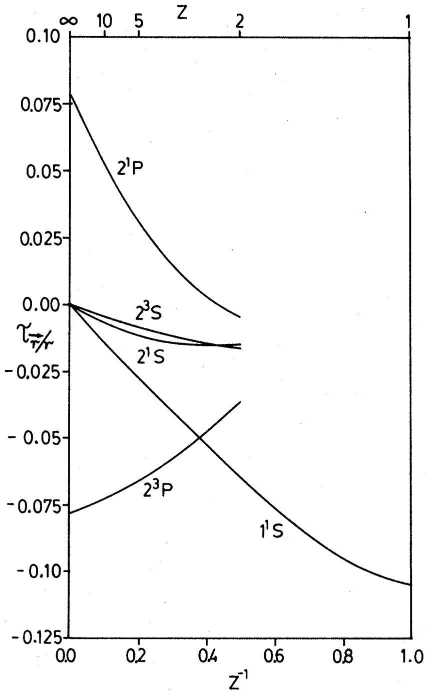

FIG. 3. Angular correlation coefficients.

Kutzelnigg and his colleagues[7] proposed a restatement of Hund's rule in the form: For a given orbital configuration, the spin multiplicity with the lowest energy will exhibit the most negative angular correlation effects. Banyard and Ellis[21] subsequently confirmed this for the $2\,{}^1P$ and $2\,{}^3P$ states of the helium atom. Figures 2 and 3 show that the reformulation is indeed valid for the $2\,{}^1P$ and $2\,{}^3P$ states of the entire two-electron isoelectronic series, and for the $2\,{}^1S$ and $2\,{}^3S$ states of the neutral helium atom. However, the figures make it equally clear that the restatement is *not valid* for the $2\,{}^1S$ and $2\,{}^3S$ states of the two-electron isoelectronic series for $Z > 2$.

The tables and figures show that positive values are found for the $2\,{}^1P$ angular correlation coefficients for $Z > 2$. This confirms the general prediction by Kutzelnigg and co-workers[7] that positive correlation coefficients may be found in excited states. However, their specific predictions[7] that positive $\tau_{\bar{r}}$ values would be found for the $2\,{}^1P$ and $2\,{}^1S$ states of neutral He are seen to be incorrect. The present results for the $2\,{}^1P$ state of He support the calculations of Banyard and Ellis[21] who showed that Hartree-Fock wave functions, and more generally wave functions based on $(s,p)$ configurations only, predict positive $\tau_{\bar{r}}$ values, but more accurate wave functions which allow for $(s,p)/(d,p)$ interactions predict negative $\tau_{\bar{r}}$ values for the $2\,{}^1P$ state of neutral He. This is another instance where the atoms at the low nuclear-charge end of an isoelectronic sequence behave differently from the rest.[22] The positive correlation coefficients in the $2\,^1P$ state indicate that the electrons tend to stay on the same side of the nucleus. This is consistent with the fact that screening of the nucleus by an electron is more pronounced in the singlet than in the triplet[23] which has negative correlation coefficients. Perhaps a detailed examination of the pair correlation densities in these excited states of helium would enable one to find a consistent reformulation of Hund's rules.

## ACKNOWLEDGMENT

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[5] McWeeny's correlation factor (Ref. 2) $f(\vec{r}_1,\vec{r}_2)$ is related to the pair correlation density $c(\vec{r}_1,\vec{r}_2)$ by the equation

$$c(\vec{r}_1,\vec{r}_2)=D_1(\vec{r}_1)\,D_1(\vec{r}_2)f(\vec{r}_1,\vec{r}_2)+D_2(\vec{r}_1,\vec{r}_2)/n\,.$$

The second term on the right-hand side appears because McWeeny's one- and two-electron densities are normalized to $n$ and $n(n-1)$, respectively, as opposed to the unit normalization adopted in this paper. Note, in particular, that

$$\int c(\vec{r}_1,\vec{r}_2)\,d\vec{r}_1=\int c(\vec{r}_1,\vec{r}_2)\,d\vec{r}_2=0,$$

but that

$$\int D_1(\vec{r}_1)f(\vec{r}_1,\vec{r}_2)\,d\vec{r}_1=\int D_1(\vec{r}_2)f(\vec{r}_1,\vec{r}_2)\,d\vec{r}_2=-1/n\,.$$

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