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Angular-correlation coefficients for first-row atoms

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It is shown that a statistical angular-correlation coefficient τ may be obtained from the small-momentum-transfer behavior of x-ray and high-energy electron-scattering intensities. Published tables of these quantities are exploited to obtain values of τ for correlated wave functions of first-row atoms and ions. τ is negligibly small in lithium, about -0.09 in beryllium, and its magnitude decreases monotonically as one goes across the first row from Be to Ne.

INTRODUCTION

The term electron correlation has two common meanings. In the traditional quantum chemistry sense electron correlation effects are those due to the difference between the exact and the Hartree-Fock electron pair densities.[1] In the statistical sense electron correlation effects are those due to the difference between the true electron pair density and the product of the true one-electron densities.[2] These two notions of electron correlation are different because the antisymmetry of the Hartree-Fock wave function accounts for the Fermi correlation between electrons of like spin. The term electron correlation will be used in the statistical sense throughout this paper.

Statistical electron correlation can be studied by a detailed examination of correlation factors and holes[2] or pair correlation densities.[3] However, all these quantities are complicated[4] functions of up to six variables. Hence, it is convenient to have numerical indices which provide overall measures of the statistical correlation. The correlation coefficients introduced by Kutzelnigg, Del Re, and Berthier[5] serve this purpose admirably. A detailed study of correlation coefficients in the five lowest states of the heliumlike ions has been carried out recently.[3] The K- and L-shell components of the correlation coefficients in the berylliumlike ions have also been studied.[6]

In this paper it is shown how an angular-correlation coefficient may be extracted from x-ray and high-energy electron-scattering intensities. The method is then utilized to calculate and study angular-correlation coefficients for the first-row atoms and ions.

ANGULAR CORRELATION AND SCATTERING INTENSITIES

One possible angular-correlation coefficient[5] that is suitable for atoms may be defined by

$$\tau=2\left\langle \sum_{i>j} \vec{r}_i\cdot\vec{r}_j \right\rangle \bigg/ (N-1)\left\langle \sum_i r_i^2 \right\rangle,$$

where N is the number of electrons. τ is bounded in magnitude by unity:

$$-1\leq\tau\leq 1.$$

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. The vanishing of the statistical pair correlation density is a *sufficient but not necessary* condition for τ to be zero.

The expectation value

$$S_{-1}=2\left\langle \sum_{i,j} \vec{r}_i\cdot\vec{r}_j \right\rangle \bigg/ 3$$

can be used to rewrite τ in the form

$$\tau=\left[3S_{-1}\bigg/2\left\langle \sum_i r_i^2 \right\rangle-1\right]\bigg/(N-1).$$

This implies[3] that τ can be calculated from experimental data because $\langle \sum_i r_i^2 \rangle$ can be obtained from the diamagnetic susceptibility and S_{-1} can be obtained from the dipole oscillator strength distribution by virtue of the sum rule[7]

$$S_{-1}=\sum_{n} f_{0n}E_{0n}^{-1},$$

where f_{0n} is the spherically averaged dipole oscillator strength for the transition from the ground state to the nth state, and E_{0n} is the corresponding transition energy.

X-ray and high-energy electron-scattering intensities can also be used to obtain τ. Within the context of Waller-Hartree theory[8] the coherent (I^{x}_{coh}) and incoherent (I^{x}_{inc}) x-ray scattering intensities are given by

$$I^{x}_{\mathrm{coh}}(\mu)/I^{x}_{\mathrm{cl}}=|F(\mu)|^2$$

and

$$I^{x}_{\mathrm{inc}}(\mu)/I^{x}_{\mathrm{cl}}=S(\mu),$$

where $F(\mu)$ is the form factor, $S(\mu)$ is the incoherent scattering function, μ is the momentum transfer, and I^{x}_{cl} is the classical expression for the total intensity of radiation scattered by a free electron initially at rest. Moreover, within the context of the first Born and binary-encounter approximations,[8] the elastic (I^{e}_{el}) and inelastic (I^{e}_{in}) intensities for high-energy electron scattering from free atoms may be expressed as

$$I^{e}_{\mathrm{el}}(\mu)/I^{e}_{\mathrm{cl}}=4\mu^{-4}[N-F(\mu)]^2$$

and

$$I^{e}_{\mathrm{in}}(\mu)/I^{e}_{\mathrm{cl}}=4\mu^{-4}S(\mu),$$

where I^{e}_{cl} is the Rutherford expression. The small-μ expansion[8] for $F(\mu)$ is given by

$$F(\mu)=N-\left\langle\sum_i r_i^2\right\rangle\mu^2/6+a_4\mu_4+a_6\mu^6+\cdots$$

and the small-μ expansion[8] for $S(\mu)$ is given by

$$\mu^{-2}S(\mu)=S_{-1}/2+b_2\mu^2+b_4\mu^4+\ldots .$$

Thus, it is clear that $\langle\sum_i r_i^2\rangle$ and S_{-1} may be obtained from the zero-μ limit of $6[N-F(\mu)]\mu^{-2}$ and $2S(\mu)\mu^{-2}$, respectively.

FIRST-ROW ATOMS

Tanaka and Sasaki[9] have tabulated values of $F(\mu)$ and $S(\mu)$ calculated from valence-shell configuration-interaction (CI) wave functions for a variety of first-row atoms and ions. Values of S_{-1} and $\langle\sum_i r_i^2\rangle$ were extracted from their data by fitting polynomials in μ^2 to $2S(\mu)\mu^{-2}$ and $6[N-F(\mu)]\mu^{-2}$, respectively. One value of each of the quantities was obtained by fitting polynomials of the form $a+b\mu^2$ to the data points at $\mu a_0=0.1$ and 0.2. Another value of each of the quantities was obtained by fitting polynomials of the form $a+b\mu^2+c\mu^4$ to the data points at $\mu a_0=0.1$, 0.2, and 0.3. The requisite expectation values for the berylliumlike ions have also been tabulated[6] for 55-term CI wave functions,[10] and for 10-term multiconfiguration self-consistent field (MCSCF) wave functions.[11] SCF values[12] and a few others[13,14] were also used.

Values of S_{-1}, $\langle\sum_i r_i^2\rangle$, and τ are listed in Table I for the neutral first-row atoms, in Table II for the berylliumlike ions, and in Table III for the neonlike ions. The close agreement between values obtained by two- and three-point fits to the form factors and incoherent scattering factors encourages the belief that the fitting provides reliable results. Some of the discrepancies between the 10-term MCSCF values[11] and the 55-term CI values[6] for the four-electron ions may be due to the fact that the latter were not computed directly but via a cluster expansion truncated after the pair terms.[6]

τ is zero for Li and Be in the Hartree-Fock approximation because the latter involves only s orbitals in these atoms. In lithium the true K-shell value of τ could be expected to be close to the corresponding value[3] of -0.039 in Li^{+}. However, since the two intershell pairs can be expected[15,16] to be virtually uncorrelated, the overall value of τ is rather small in magnitude as the 45-term CI values of -0.0032 indicates. In beryllium the K-shell value[6] of τ is -0.0296 which is close to the value[3] of $-0.029\,76$ in Be^{2+}, the L-shell value[6] is -0.299, and the intershell values are negligible.[6] The overall value of τ is substantial (-0.09) primarily because of the strong L-shell angular correlation which arises because of the well-known[16,17] $2s-2p$ near degeneracy. In the infinite nuclear charge limit of the beryllium isoelectronic series the near degeneracy becomes a true degeneracy, the exact wave function approaches the limit

$$\psi=a\,|1s\overline{1s}2s\overline{2s}|+(1-a^2)^{1/2}(|1s\overline{1s}2p_{+}\overline{2p}_{-}|-|1s\overline{1s}\overline{2p}_{+}2p_{-}|-|1s\overline{1s}2p_{0}\overline{2p}_{0}|)/\sqrt{3},$$

and the overall angular-correlation coefficient approaches the limiting value of $-0.051\,781$. In the

TABLE I. Angular-correlation coefficients for the first-row atoms.

Atom and state	Wave function	S_{-1}/a_0^2	$\left\langle \sum_i r_i^2 \right\rangle / a_0^2$	τ
Li ^2S	SCF[a]	12.42	18.63	0
	45-term CI[b]	12.17	18.37	−0.0032
Be ^1S	SCF[a]	11.55	17.32	0
	10-term MCSCF[c]	8.063	16.30	−0.0860
	37-term CI[d]	8.849	17.02	−0.0734
	55-term CI[e]	7.686	16.30	−0.0975
	7-term *L*-shell CI[f]	8.283	17.00	−0.0897
	7-term *L*-shell CI[g]	8.279	17.05	−0.0905
B ^2P	SCF[a]	8.703	15.85	−0.0441
	21-term *L*-shell CI[f]	7.033	15.65	−0.0815
	21-term *L*-shell CI[g]	7.022	15.64	−0.0816
C ^3P	SCF[a]	6.847	13.79	−0.0511
	37-term *L*-shell CI[f]	6.050	13.85	−0.0690
	37-term *L*-shell CI[g]	6.059	13.85	−0.0688
C ^1D	34-term *L*-shell CI[f]	6.483	14.45	−0.0654
	34-term *L*-shell CI[g]	6.508	14.44	−0.0648
C ^1S	21-term *L*-shell CI[f]	6.883	15.75	−0.0689
	21-term *L*-shell CI[g]	6.903	15.79	−0.0688
N ^4S	SCF[a]	5.610	12.08	−0.0506
	21-term *L*-shell CI[f]	5.250	12.00	−0.0573
	21-term *L*-shell CI[g]	5.263	11.99	−0.0569
N ^2D	60-term *L*-shell CI[f]	5.450	12.65	−0.0590
	60-term *L*-shell CI[g]	5.463	12.66	−0.0588
N ^2P	62-term *L*-shell CI[f]	5.417	12.55	−0.0588
	62-term *L*-shell CI[g]	5.412	12.51	−0.0585
O ^3P	SCF[a]	5.036	11.17	−0.0463
	67-term *L*-shell CI[f]	4.600	11.50	−0.0571
	67-term *L*-shell CI[g]	4.591	11.54	−0.0576
O ^1D	53-term *L*-shell CI[f]	4.833	11.45	−0.0524
	53-term *L*-shell CI[g]	4.840	11.47	−0.0524
O ^1S	28-term *L*-shell CI[f]	4.800	11.30	−0.0518
	28-term *L*-shell CI[g]	4.791	11.23	−0.0514

TABLE I. *(Continued).*

F ^2P	SCF[a]	4.513	10.24	−0.0423
	57-term L-shell CI[f]	4.200	10.20	−0.0478
	57-term L-shell CI[g]	4.191	10.19	−0.0479
Ne ^1S	SCF[a]	4.055	9.376	−0.0390
	18-term L-shell CI[f]	3.800	9.700	−0.0458
	18-term L-shell CI[g]	3.793	9.747	−0.0463

[a] See Reference 12.
[b] Wave function from Ref. 10 (see Ref. 13 for expectation values).
[c] Reference 11.
[d] Wave function from Ref. 14 and expectation values from Ref. 11.
[e] Wave function from Ref. 10 and expectation values from Ref. 6.
[f] Expectation values from the two-point fit to the $F(\mu)$, $S(\mu)$ data of Ref. 9. See text.
[g] Expectation values from the three-point fit to the $F(\mu)$, $S(\mu)$ data of Ref. 9. See text.

atoms from B through Ne there is an angular Fermi correlation between the s and p electrons in addition to the $2s-2p$ near-degeneracy effects found in B ^2P, C ^3P, C ^1D, C ^1S, and N ^2P. As one moves across the first row from B to Ne the angular Fermi correlation becomes more important and the near-degeneracy effects become less important and even vanish as in N ^4S, N ^2D, O, F, and Ne. The overall result is a steady decrease in the magnitude of τ from Be through Ne.

Table I shows that for states arising from the same configuration τ does not vary greatly, and its ordering does not always correspond to the energy ordering. These results along with eariler work,[3] show that τ is of limited value in discussions of Hund's rule,[5,3,18] especially when the electrons in

TABLE II. Angular-correlation coefficients for the beryllium isoelectronic series.

Z	Wave function	S_{-1}/a_0^2	$\left\langle \sum_i r_i^2 \right\rangle / a_0^2$	τ
3	10-term MCSCF[a]	32.86	68.73	−0.0943
	55-term CI[b]	23.63	58.75	−0.1322
4	10-term MCSCF[a]	8.063	16.30	−0.0860
	55-term CI[b]	7.686	16.30	−0.0975
5	10-term MCSCF[a]	3.892	7.668	−0.0795
	55-term CI[b]	3.806	7.677	−0.0854
6	10-term MCSCF[a]	2.318	4.489	−0.0752
7	10-term MCSCF[a]	1.555	2.973	−0.0718
8	10-term MCSCF[a]	1.115	2.113	−0.0694
	55-term CI[b]	1.129	2.123	−0.0674
∞	Exact	0	0	−0.0518

[a] Reference 11.
[b] Wave function from Ref. 10 and expectation values from Ref. 6.

TABLE III. Angular-correlation coefficients for the neon isoelectronic series.

Z	Wave function	S_{-1}/a_0^2	$\left\langle \sum_i r_i^2 \right\rangle / a_0^2$	τ
9	18-term L-shell CI[a]	7.233	16.30	-0.0372
	18-term L-shell CI[b]	7.227	16.33	-0.0374
10	18-term L-shell CI[a]	3.800	9.700	-0.0458
	18-term L-shell CI[b]	3.793	9.747	-0.0463
11	18-term L-shell CI[a]	2.633	6.650	-0.0451
	18-term L-shell CI[b]	2.647	6.670	-0.0450
∞	Exact	0	0	-0.0472

[a] Expectation values from the two-point fit to the $F(\mu)$, $S(\mu)$ data of Ref. 9 (see text).
[b] Expectation values from the three-point fit to the $F(\mu)$, $S(\mu)$ data of Ref. 9 (see text).

unfilled subshells all have the same l value.

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

$$\tau = c_0 + c_1 Z^{-1} + c_2 Z^{-2} + \cdots .$$

For the ground (1^1S) state of the heliumlike ions,[3] $c_0 = 0$, $c_1 = -0.126$, and $c_2 = +0.024$. It is easy to show that $c_0 = -0.0518$ for the ground (^1S) state of the four-electron ions. Moreover, a least-squares fit to the ten-term MCSCF values of τ listed in Table II yields $c_1 = -0.145$ and $c_2 = +0.032$ for the beryllium isoelectronic series. It may be shown that $c_0 = -0.0472$ for the ground state of the neonlike ions. Although there is insufficient data in Table III to extract a meaningful value of c_1 it seems plausible that c_1 will turn out to be positive in this case.

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[1] O. Sinanoglu and K. A. Brueckner, *Three Approaches to Electron Correlation in Atoms* (Yale University Press, New Haven, Conn., 1970); A. C. Hurley, *Electron Correlation in Small Molecules* (Academic, London, 1976).

[2] R. McWeeny, Rev. Mod Phys. 32, 335 (1960); Int. J. Quantum Chem. Symp. 1, 351 (1967).

[3] A. J. Thakkar and V. H. Smith Jr., Phys. Rev. A 23, 473 (1981).

[4] Some idea of the complexity of the pair correlation density can be obtained by examining detailed cross-sectional diagrams of the correlation factor such as those given by V. Maslen, Proc. Phys. Soc. London Sect. A 69, 734 (1956); G. Sperber, Int. J. Quantum Chem. 5, 189 (1971); 6, 881 (1972); M. A. Besson and M. Suard, *ibid.* 10, 151 (1976); G. Doggett, Mol. Phys. 34, 1739 (1977); I. L. Cooper and C. N. M. Pounder, Int. J. Quantum Chem. 17, 759 (1980).

[5] W. Kutzelnigg, G. Del Re, and G. Berthier, Phys. Rev. 172, 49 (1968).

[6] K. E. Banyard and M. M. Mashat, J. Chem. Phys. 67, 1405 (1977).

[7] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Gottingen, 1957), pp. 357–358.

[8] R. A. Bonham and M. Fink, *High-Energy Electron Scattering* (Van Nostrand, New York, 1974). A concise summary of the relevant equations may be found in A. J. Thakkar and V. H. Smith, Jr., J. Phys. B 11, 3803 (1978).

[9] K. Tanaka and F. Sasaki, Int. J. Quantum Chem. 5, 157 (1971).

[10] A. W. Weiss, Phys. Rev. 122, 1826 (1961).

[11] N. Sabelli and J. Hinze, J. Chem. Phys. 50, 684 (1969). The values reported for $\langle \sum_{i \neq j} \vec{r}_i \cdot \vec{r}_j \rangle$ were multiplied by a factor of 2 in order to make them consistent with values from other sources.

[12] Values of S_{-1} were taken from F. W. Cummings, J. Chem. Phys. 63, 4960 (1975) who computed them from the SCF wave functions reported by E. Clemen-

ti, IBM J. Res. Dev. 9, 2 (1965). Values of $\langle \sum_i r_i^2 \rangle$ were taken from R. J. Boyd, Can. J. Phys. 55, 452 (1977) who computed them from the SCF wave functions reported by E. Clementi and C. Roetti, At. Data Nucl. Data Tables 14, 177 (1974). It is felt that these two sets of SCF wave functions are of sufficiently similar quality that this procedure does not lead to any inconsistency which is significant in the present context.

[13] S_{-1} for Li was computed by G. M. Stacey and A. Dalgarno, J. Chem. Phys. 48, 2515 (1968). $\langle \sum_i r_i^2 \rangle$ was computed by K. E. Banyard, M. Dixon, and A. D. Tait, Phys. Rev. A 4, 2199 (1971); see also V. H. Smith Jr., R. E. Brown, and A. J. Thakkar, *ibid.* 7, 1192 (1973).

[14] R. E. Watson, Phys. Rev. 119, 170 (1960).

[15] C. Froese Fischer, Int. J. Quantum Chem. 9, 273 (1975).

[16] J. Linderberg and H. Shull, J. Mol. Spectrosc. 5, 1 (1960).

[17] V. V. Kibartas and A. P. Yutsis, Zh. Eksp. Teor. Fiz. 25, 264 (1953).

[18] K. E. Banyard and D. J. Ellis, J. Phys. B 8, 2311 (1975).