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REGULAR ARTICLE

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Multipole analysis of electron repulsion energies in many-electron atoms

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Abstract The repulsion energy W between two electrons located at $\mathbf{r}_1$ and $\mathbf{r}_2$ can be expressed by the sum of the interaction energies W_k between an electron located at $\mathbf{r}_>$ and linear electric multipoles located at the coordinate origin along the vector $\mathbf{r}_<$, where $\mathbf{r}_<$ and $\mathbf{r}_>$ are the vectors with smaller and larger moduli, respectively, of the two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. All the existing multipole contributions W_k to the Hartree–Fock electron repulsion energy W are examined for the 102 atoms He through Lr in their ground states. It is found that $|W_k|$ decreases rapidly with increasing k, $W_0 > W$, and W_k with $k \geq 1$ work to reduce W_0. The effect of electron correlation is also discussed for some helium-like atoms.

Keywords Multipole contributions · Electron repulsion energies · Correlation effects · Atoms

1 Introduction

The multipole expansion (see, e.g., Ref. [1]) of the reciprocal distance $r_{12}^{-1} = |\mathbf{r}_1 - \mathbf{r}_2|^{-1}$ between two electrons at $\mathbf{r}_1$ and $\mathbf{r}_2$ reads

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} P_k(\cos\theta_{12}), \tag{1}$$

where $r_< = \min(r_1, r_2)$, $r_> = \max(r_1, r_2)$, θ_{12} is the angle between the vectors $\mathbf{r}_1$ and $\mathbf{r}_2$, and $P_k(x)$ is the Legendre function of the first kind. Accordingly, the electron repulsion energy $W =< r_{12}^{-1} >$ in Hartree atomic units is given by

$$W = \sum_{k=0}^{\infty} W_k, \tag{2a}$$

$$W_k = \left\langle \frac{r_<^k}{r_>^{k+1}} P_k(\cos\theta_{12}) \right\rangle, \tag{2b}$$

where the angular brackets for a two-electron function $f(\mathbf{r}_1, \mathbf{r}_2)$ stand for

$$< f(\mathbf{r}_1, \mathbf{r}_2) >= \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 f(\mathbf{r}_1, \mathbf{r}_2) \Gamma(\mathbf{r}_1, \mathbf{r}_2), \tag{3}$$

in which $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is the spinless two-electron density function normalized to the number of electron pairs. Equation 2a and 2b implies that the electrostatic repulsion energy between two electrons located at $\mathbf{r}_1$ and $\mathbf{r}_2$ is equivalent to the sum of the interaction energies between an electron located at $\mathbf{r}_>$ and linear electric multipoles located at the coordinate origin along the vector $\mathbf{r}_<$, where $\mathbf{r}_<$ and $\mathbf{r}_>$ are the vectors with smaller and larger moduli, respectively, of the two vectors $\mathbf{r}_1$ and $\mathbf{r}_2$. Specifically, the summands W_k in Eq. 2a with $k = 0, 1, 2$, and 3 correspond to the monopole, dipole, quadrupole, and octupole contributions, respectively.

In a recent study of the splitting of the atomic radial density functions into the inner and outer densities, it has been accidentally found [2] that the monopole contribution $W_0 =< r_>^{-1} >$, which is the minus first moment of the outer radial density, is a good approximation to the electron repulsion energy $W =< r_{12}^{-1} >$ for ground-state atoms within the Hartree–Fock framework. It is also known [3] that $< r_{12}^{-1} > = < r_>^{-1} >$ precisely for the helium-like atoms if both electrons are in s orbitals and a single-configuration approximation is applied. Accordingly, model helium-like atoms were discussed [4–6], in which the electron repulsion energy operator r_{12}^{-1} is simply approximated by $r_>^{-1}$. The observations [2,3] have raised questions (1) whether an infinite number of multipoles actually contribute to the electron repulsion energy W as Eq. 2a apparently shows, (2) whether all the multipole contributions W_k are positive, and (3) how are the relative magnitudes of W_k when k is varied? Since the electron repulsion energy W is a nontrivial component of the total energy and its multipole analysis can be a useful tool for problems where W plays an important role, the clarification of the above questions would be helpful for our fundamental knowledge. In the present paper, we examine all the existing multipole contributions W_k to the Hartree–Fock electron repulsion energy W for the 102 atoms He through Lr in their

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ground states. When these atoms are concerned, it will be found that only W_k with $k \leqslant 6$ are nonvanishing, W_0 is the dominant term slightly greater than W, and negative W_k with $1 \leqslant k \leqslant 6$ work to reduce W_0. The effect of electron correlation is also discussed for some helium-like atoms. Hartree atomic units are used throughout.

2 Multipole contributions in many-electron atoms

For a determinantal wave function composed of a set of orthonormal spin-orbitals $\psi_a(\mathbf{r})\eta_a(s)$, the spinless two-electron density function $\Gamma(\mathbf{r}_1, \mathbf{r}_2)$ is expressed as

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \sum_{a,b,c,d} C_{abcd}\psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2)\psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2), \qquad (4)$$

where C_{abcd} are expansion coefficients which include the spin integrals $\int \mathrm{d}s\eta_a^*(s)\eta_c(s)$ and $\int \mathrm{d}s\eta_b^*(s)\eta_d(s)$ with s being the spin coordinate. Therefore, the 2^k pole contribution W_k is given by

$$W_k = \sum_{a,b,c,d} C_{abcd} W_k^{abcd}, \qquad (5a)$$

$$W_k^{abcd} = \int \mathrm{d}\mathbf{r}_1 \mathrm{d}\mathbf{r}_2 \psi_a^*(\mathbf{r}_1)\psi_b^*(\mathbf{r}_2) \times \frac{r_<^k}{r_>^{k+1}} P_k(\cos\theta_{12})\psi_c(\mathbf{r}_1)\psi_d(\mathbf{r}_2). \qquad (5b)$$

In atomic systems, we can generally assume that the spatial function $\psi_a(\mathbf{r})$ is a product of the radial $R_a(r)$ and spherical harmonic $Y_a(\Omega) = Y_{l_a m_a}(\Omega)$ functions, where (r, Ω) with $\Omega = (\theta, \phi)$ is the polar coordinates of the vector $\mathbf{r}$. Then, Eq. 5b is simplified to

$$W_k^{abcd} = Q_k(a, b; c, d)A_k(a, b; c, d), \qquad (6a)$$

where

$$Q_k(a, b; c, d) = \int_0^\infty \mathrm{d}r_1 \int_0^\infty \mathrm{d}r_2 r_1^2 r_2^2 R_a^*(r_1)R_b^*(r_2) \times \frac{r_<^k}{r_>^{k+1}} R_c(r_1)R_d(r_2), \qquad (6b)$$

$$A_k(a, b; c, d) = \int \mathrm{d}\Omega_1 \mathrm{d}\Omega_2 Y_a^*(\Omega_1)Y_b^*(\Omega_2) \times P_k(\cos\theta_{12})Y_c(\Omega_1)Y_d(\Omega_2). \qquad (6c)$$

Since an addition theorem (see, e.g., Ref. [1]) states that

$$P_k(\cos\theta_{12}) = \frac{4\pi}{2k+1} \sum_{m=-k}^{k} Y_{km}^*(\Omega_1)Y_{km}(\Omega_2), \qquad (7)$$

the two-electron angular integral 6c is calculated to be

$$A_k(a, b; c, d) = \delta_{m_a+m_b, m_c+m_d} c^k(a, c)c^k(d, b), \qquad (8a)$$

where δ_{ij} is the Kronecker delta and $c^k(a, b) = c^k(l_a m_a, l_b m_b)$ is the Condon–Shortley parameter [7,8] defined by

$$c^k(l_a m_a, l_b m_b) = \sqrt{\frac{4\pi}{2k+1}} \int \mathrm{d}\Omega \times Y_{l_a m_a}^*(\Omega)Y_{k, m_a - m_b}(\Omega)Y_{l_b m_b}(\Omega). \qquad (8b)$$

Due to the property [7,8] of $c^k(a, b)$, the angular integral $A_k(a, b; c, d)$ vanishes unless the following four conditions are satisfied simultaneously:

$$k + l_a + l_c = \text{even integer}, \quad k + l_b + l_d = \text{even integer},$$

$$|l_a - l_c| \leqslant k \leqslant l_a + l_c, \quad |l_b - l_d| \leqslant k \leqslant l_b + l_d. \qquad (9)$$

Therefore, all the multipole contributions W_k in Eq. 2a, 2b disappear for $k > 2l_{\max}$, where $l_{\max}$ is the largest azimuthal quantum number appearing in spatial functions. When only s orbitals are involved, as in the cases of He, Li, and Be atoms in the Hartree–Fock and radially correlated approximations, it follows that only the monopole contribution W_0 is nonvanishing and hence $W = W_0$.

3 Numerical results and discussion

The experimental ground electronic configurations and LS terms [9] were considered for all the 102 atoms He (atomic number $Z = 2$) through Lr ($Z = 103$). For these states, the radial functions $R_a(r)$ were generated by the numerical Hartree–Fock method based on a modified version of the MCHF72 program [10]. Equations 6b and 8a were then used to compute the contributions of various sets of spin-orbitals to W_k, where the $c^k(a, b)$ values were taken from Refs. [7,8].

Table 1 exemplifies the nonzero multipole contributions W_k for the six group-18 atoms. Since orbitals with g or higher azimuthal quantum numbers are not occupied, W_k with $k \geq 7$ do not appear. In the table, we find that (1) $W \leq W_0$, where the equality holds for the He atom with $l_{\max} = 0$, (2) $W_k < 0$ when $k \geq 1$, and (3) $|W_k| > |W_{k+1}|$. In particular, we have $W_0 >> |W_1|$. These observations are common to all the atoms examined. The equality in (1) is found for the Li and Be atoms additionally, where only s orbitals are occupied. The results confirm the literature statement [2] that $W \cong W_0$ yet point out that W_0 is never smaller than W. Concerning the point (2), we note that this is not always true when excited states are considered. A simple example is the C atom with the ground $2s^2 2p^2$ configuration. The quadrupole contribution W_2 is negative for the ground ^3P term but is positive for the excited ^1D and ^1S terms, though the inequality $W \leq W_0$ remains unaltered.

For the 102 atoms in their ground states, Fig. 1 plots the nonvanishing multipole contributions W_k ($k = 0 - 6$) as a function of atomic number Z. (The electron repulsion energy W cannot be distinguished from the monopole contribution W_0 in the present scale of the figure.) We find all the multipole contributions monotonically increase in their magnitudes with increasing Z, though the increment is not always smooth. In particular, the nonsmooth increases are

Table 1 Nonvanishing multipole contributions for the six group-18 atoms

Multipole contribution	He	Ne	Ar	Kr	Xe	Rn
W_0	1.02577	56.04225	207.96399	1108.34723	2765.84821	8409.87250
W_1		−1.49015	−4.74159	−18.34932	−37.45851	−84.87256
W_2		−0.51312	−1.79949	−8.57642	−19.01120	−47.19173
W_3				−2.22946	−6.20112	−20.39615
W_4				−0.72413	−2.25350	−9.62243
W_5						−2.87393
W_6						−0.89454
Sum = W	1.02577	54.03897	201.42290	1078.46789	2700.92388	8244.02117

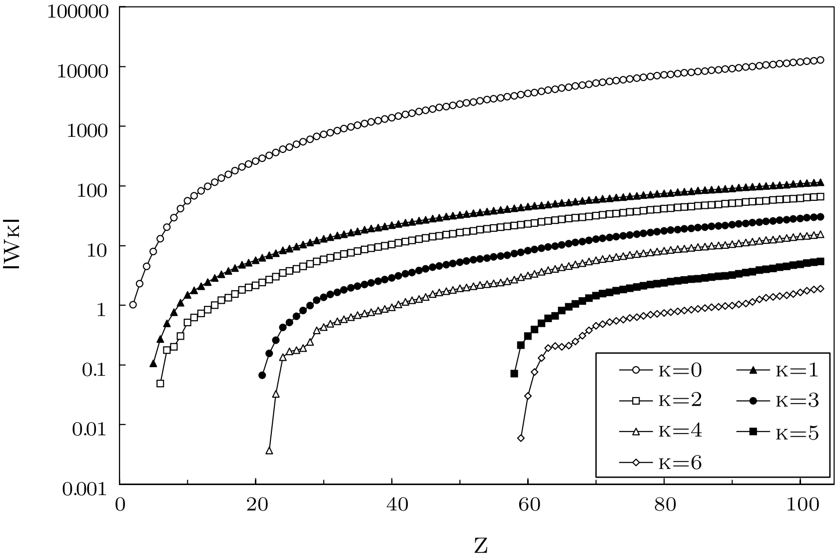

Fig. 1 The multipole contributions W_k as a function of atomic number Z. The electron repulsion energy W is superimposed on the monopole contribution W_0 in this scale of the figure

remarkable in $|W_k|$ with $k = 2, 4,$ and 6 for first several atoms, but the physical reason remains unclear. Since the ordinate of the figure is logarithmic, it is very clear that $W_0 >> |W_1| > |W_2| > \cdots > |W_6|$ with no exceptions: The contribution $|W_k|$ diminishes rapidly with increasing k. Table 2 summarizes the minimum, average, and maximum ratios $|W_k|/W$ for the 102 atoms. The monopole contribution W_0 is quite dominant, as mentioned above, and the next largest dipole contribution W_1 is only 1.5% of the electron repulsion energy W when averaged over the 102 atoms.

Table 2 Ratios of the multipole contributions W_k relative to the electron repulsion energy W

Ratio	No. of atoms	Minimum	Average	Maximum
W_0/W	102	1.00000 (He,Li,Be)	1.02432	1.03707 (Ne)
$-W_1/W$	99	0.00914 (Lr)	0.01529	0.02763 (F)
$-W_2/W$	98	0.00381 (C)	0.00703	0.00950 (Ne)
$-W_3/W$	83	0.00024 (Sc)	0.00222	0.00250 (Pt)
$-W_4/W$	82	0.00001 (Ti)	0.00092	0.00123 (Lr)
$-W_5/W$	46	0.00002 (Ce)	0.00030	0.00043 (Lr)
$-W_6/W$	45	0.00000 (Pr)	0.00010	0.00015 (Lr)

The parentheses show the atoms for which the minimum or maximum ratio is observed

To examine the electron correlation effect on the multipole contributions W_k, we have next performed multi configuration Hartree–Fock calculations for selected helium-like atoms, using a modified version of the MCHF88 program [11] and the best combination of 30 configurations [12,13] with $l_{\max} = 8$. The present calculations reproduce more than 99%, ranging from 99.4% ($Z = 100$) to 99.9% ($Z = 1$), of the correlation energies.

For $Z = 1(\mathrm{H}^-)$, 2 (He), 3 (Li^+), 5 (B^{3+}), 10 (Ne^{8+}), 50 (Sn^{48+}), and 100 (Fm^{98+}), Table 3 summarizes the correlated electron repulsion energies W and their multipole components W_k which are greater than 5×10^{-6} in magnitudes. The corresponding Hartree–Fock values are also listed for comparison. The two sets of W values are well approximated by linear functions of Z (the correlation coefficients are 1.000000 in both cases) with the slope +5/8, which appears as the first-order correction in the Z-perturbation treatment [14] of the total energies of the two-electron atoms. However, we find that the correlated W is always smaller than the Hartree–Fock W. Except for the H^- ion (−0.08453), the difference ΔW between the correlated and Hartree–Fock W decreases with increasing Z from −0.07981 ($Z = 2$) to −0.09251 ($Z = 100$). The Z dependence of the difference ΔW is analogous to that of the correlation energy ΔE for

Table 3 Multipole analysis of the electron repulsion energies W for some helium-like atoms. The multipole components W_k greater than 5×10^{-6} in magnitudes are shown for the correlated results

Multipole contribution	$Z = 1$	2	3	5	10	50	100
Hartree–Fock							
$W_0 = W$	0.39548	1.02577	1.65169	2.90228	6.02766	31.02793	62.27796
Correlated							
W_0	0.33721	0.99297	1.62083	2.87248	5.99849	30.99920	62.24928
W_1	−0.02439	−0.04112	−0.04533	−0.04849	−0.05076	−0.05252	−0.05274
W_2	−0.00139	−0.00426	−0.00537	−0.00631	−0.00703	−0.00763	−0.00770
W_3	−0.00031	−0.00103	−0.00135	−0.00164	−0.00186	−0.00206	−0.00208
W_4	−0.00011	−0.00037	−0.00049	−0.00059	−0.00068	−0.00076	−0.00077
W_5	−0.00004	−0.00015	−0.00020	−0.00025	−0.00029	−0.00032	−0.00032
W_6	−0.00002	−0.00006	−0.00008	−0.00010	−0.00012	−0.00013	−0.00014
W_7		−0.00002	−0.00003	−0.00004	−0.00004	−0.00005	−0.00005
W_8		−0.00001	−0.00002	−0.00002	−0.00002	−0.00003	−0.00003
W	0.31095	0.94596	1.56797	2.81505	5.93767	30.93571	62.18546

$Z = 2 - 100$, and both ΔW and ΔE are almost constant for large Z. The correlation coefficient between the two properties is calculated to be 0.999875.

The multipole analysis shows that in all the atoms, the reduced electron repulsion energies by the electron correlation are attributed to the reduction ΔW_0 in the monopole component and the appearance of negative higher multipole contributions W_k ($k \geq 1$). Since $W_0 =< r_>^{-1} >$, the reduced ΔW_0 is in accord with the known result [15] that the outer radius $< r_> >$ increases when the electron correlation is incorporated. The monopole reduction ΔW_0 and the dipole W_1 contribution are essential in the correlation effect, though the relative significance of these two contributions depends on Z. For the atoms with $Z \geq 2$, the negative dipole term W_1 contributes more to ΔW than ΔW_0, ranging from 51.5% ($Z = 2$) to 57.0% ($Z = 100$) of ΔW. In the case of $Z = 1$, on the other hand, ΔW_0 is more important than W_1 and accounts for 68.9% of ΔW. The peculiarity for the H^- ion reflects the literature observation (Ref. [16] and the references therein) that the radial correlation, against the angular correlation, is more important for H^- than for He and heavier ions.

4 Summary

The repulsion energy W between two electrons located at $\mathbf{r}_1$ and $\mathbf{r}_2$ is expressed by the sum of the interaction energies W_k between an electron located at $\mathbf{r}_>$ and linear electric multipoles located at the coordinate origin along the vector $\mathbf{r}_<$. The detailed formulas of W_k have been presented for determinantal wave functions of many-electron systems. All the existing multipole contributions W_k to the Hartree–Fock electron repulsion energy W have been examined for the 102 atoms He through Lr in their ground states. The effect of electron correlation has also been discussed for some helium-like atoms.

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