

Nuclear Mass Effect in Many-Electron Atoms*

B. W. N. LO and S. FRAGA

Division of Theoretical Chemistry, Department of Chemistry, University of Alberta,
Edmonton 7, Alberta, Canada

Received February 23, 1972

The total nuclear mass effect, including the normal mass and the mass polarization corrections, have been evaluated, from existing analytical Hartree-Fock functions, for the positive ions, neutral systems, and negative ions of all the atoms from He through Kr. The formulation for the mass polarization effect is presented in detail.

Mit Hilfe existierender analytischer Hartree-Fock-Funktionen wurde der totale Kernmasseneffekt einschließlich der Korrekturen für normale Massen und Massenspolarisation für positive und negative Ionen und neutrale Systeme für alle Atome von He bis Kr berechnet. Der Formalismus für den Massenspolarisationseffekt wird im einzelnen dargelegt.

Introduction

The electronic state functions of atoms are determined under the assumption of an infinite nuclear mass. The corresponding energies must then be modified by inclusion of the corrections for the finite mass of the nucleus and its motion (Bethe and Salpeter [1]). These corrections, although small, give rise to the so-called mass-dependent isotopic shift, that can be observed experimentally.

The purpose of this work is to present the formulation for this correction and the numerical values obtained for all the positive ions, neutral systems, and negative ions of all the atoms from He through Kr, using existing analytical Hartree-Fock functions, in order to complete the research project¹ undertaken at this Laboratory on the determination of atomic Hartree-Fock parameters [4].

Theoretical Formulation

It is customary to consider separately the two contributions, normal mass effect and mass polarization effect, to the isotopic shift. The corresponding formulations are presented below.

Normal Mass Effect

This correction arises from the use of the Rydberg constant, R_M , for the nucleus under consideration. Taking into account that

$$R_M = [M/(m + M)] R_\infty,$$

* This work has been supported in part by the National Research Council of Canada.

¹ The complete spin-orbit and electron spin-spin contact interactions and the mass variation and Darwin relativistic corrections have been reported recently [6–8]. For details on previous work see Ref. [4].

where m and M are the masses of the electron and the nucleus, respectively, one obtains

$$\Delta E_n = - [m/(m + M)] R_\infty E_\infty$$

for the normal mass correction to the energy; E_∞ represents the electronic energy evaluated for infinite nuclear mass.

Mass Polarization Effect

The correction corresponding to this effect, also denoted as specific mass effect, is given by

$$\Delta E_s = - [2m/(m + M)] R_M \langle \Psi | \sum_{i < j} A_i \cdot A_j | \Psi \rangle,$$

where Ψ represents the total electronic function for the state under consideration and the summations extend over all the electrons in the system.

Taking into account (Innes and Ufford [5]) that

$$A = \frac{\partial}{\partial r} C^{(1)} - \frac{\sqrt{2}}{r} (C^{(1)} I)^{(1)},$$

where $C^{(1)}$ is the modified spherical harmonics tensor operator of rank 1 and I is the orbital angular momentum vector operator, one can write

$$\begin{aligned} A_i \cdot A_j = & \frac{\partial^2}{\partial r_i \partial r_j} (C_i^{(1)} \cdot C_j^{(1)}) - \frac{\sqrt{2}}{r_i} \frac{\partial}{\partial r_j} \{ (C^{(1)} I)_i^{(1)} \cdot C_j^{(1)} \} \\ & - \frac{\sqrt{2}}{r_j} \frac{\partial}{\partial r_i} \{ C_i^{(1)} \cdot (C^{(1)} I)_j^{(1)} \} + \frac{2}{r_i r_j} \{ (C^{(1)} I)_i^{(1)} \cdot (C^{(1)} I)_j^{(1)} \}. \end{aligned}$$

The general matrix element between 2-electron states may then be written as

$$\begin{aligned} \langle l_a l_b L M_L S M_S | \mathcal{A}^\dagger (A_i \cdot A_j) \mathcal{A} | l_c l_d L' M'_L S' M'_S \rangle \\ = \{ \langle A \cdot A \rangle_d + \langle A \cdot A \rangle_e \} \delta(L M_L S M_S, L' M'_L S' M'_S), \end{aligned}$$

where $\langle A \cdot A \rangle_d$ and $\langle A \cdot A \rangle_e$ stand for the direct and exchange contributions; \mathcal{A} is the antisymmetrizing operator.

Using the relation

$$\langle l | (C^{(k)} I)^{(k)} | l' \rangle = [l(l+1) - k(k+1) - l'(l'+1)] [2k(2k+2)]^{-1/2} \langle l | C^{(k)} | l' \rangle,$$

one can write for the direct contribution

$$\begin{aligned} \langle A \cdot A \rangle_d = & (-1)^{L+l_b+l_c} \begin{Bmatrix} L & l_b & l_a \\ 1 & l_c & l_d \end{Bmatrix} \langle l_a | C^{(1)} | l_c \rangle \langle l_b | C^{(1)} | l_d \rangle \\ & \{ T(ab, cd) - \frac{1}{2} [l_a(l_a+1) - l_c(l_c+1) - 2] U(ab, cd) \\ & - \frac{1}{2} [l_b(l_b+1) - l_d(l_d+1) - 2] U(ba, dc) \\ & + \frac{1}{4} [l_a(l_a+1) - l_c(l_c+1) - 2] [l_b(l_b+1) - l_d(l_d+1) - 2] Q(ab, cd) \}. \end{aligned}$$

The exchange interaction may be obtained from the above expression by exchanging first the subindices a and b and then multiplying by $(-1)^{L+S+l_a+l_b}$.

The radial integrals are defined by

$$T(ab, cd) = \int_0^\infty \int_0^\infty r_1^2 dr_1 r_2^2 dr_2 R_a(1) R_b(2) \frac{\partial^2}{\partial r_1 \partial r_2} R_c(1) R_d(2),$$

$$U(ab, cd) = \int_0^\infty \int_0^\infty r_1^2 dr_1 r_2^2 dr_2 R_a(1) R_b(2) \frac{1}{r_1} \frac{\partial}{\partial r_2} R_c(1) R_d(2),$$

$$Q(ab, cd) = \int_0^\infty \int_0^\infty r_1 dr_1 r_2 dr_2 R_a(1) R_b(2) R_c(1) R_d(2),$$

R being the radial function of the shell denoted by the subscript.

Using the generalized 2-particle coefficients of fractional parentage one can now derive the expression of the total correction for a many-electron configuration. Restricting the discussion to functions obtained within the one-electron function approximation, it is found that the intrashell interaction and the direct term of the intershell interaction vanish due to the parity restriction in the double-barred matrix elements. The interaction² between two shells, when at least one of them is closed, can be written as

$$\begin{aligned} \langle A \cdot A \rangle = & (-1)^{l_a + l_b} n_a n_b [2(2l_a + 1)(2l_b + 1)]^{-1} \langle l_a | |C^{(1)}| |l_b \rangle^2 \\ & \{ T_{ba} - \frac{1}{2} [l_a(l_a + 1) - l_b(l_b + 1) - 2] U_{ab} \\ & - \frac{1}{2} [l_b(l_b + 1) - l_a(l_a + 1) - 2] U_{ba} \\ & + \frac{1}{4} [l_a(l_a + 1) - l_b(l_b + 1) - 2] [l_b(l_b + 1) - l_a(l_a + 1) - 2] Q_{ba} \}, \end{aligned}$$

where n_a and n_b are the occupation numbers of the two shells involved. For simplicity, the notation of the radial integrals has been changed to T_{ab} , U_{ab} , and Q_{ab} , with the convention $T_{ab} = T(ab, ba)$, $U_{ab} = U(ab, ba)$, and $Q_{ab} = Q(ab, ba)$.

In order for this interaction not to vanish, it is necessary that l_a and l_b differ by ± 1 . In such a case the above expression simplifies to

$$\begin{aligned} \langle A \cdot A \rangle = & -n_l n_{l+1} (l+1) [2(2l+1)(2l+3)]^{-1} \\ & [T_{l+1, l} + (l+2) U_{l, l+1} - l U_{l+1, l} - l(l+2) Q_{l+1, l}]. \end{aligned}$$

The total interaction for the configuration considered is then obtained by summing all the intershell contributions.

Results and Discussion

The calculations have been carried out for the positive ions, neutral systems, and negative ions for all the atoms from He through Kr.

The normal mass effect has been evaluated for the most abundant isotope of each atom; for simplicity the values³ are not presented here as their calculation is straightforward. For the atoms considered here, this correction varies from 86 cm⁻¹ for He to 3996 cm⁻¹ for Kr.

² The derivation parallels that given for the electron spin-spin contact interaction [6] and for that reason it is omitted here.

³ The values for both corrections for all the systems considered are available upon request.

Table 1. Values (in a.u.) of $\langle A \cdot A \rangle$ for positive ions, neutral atoms, and negative ions

Configuration ^a	State	Positive ions		Neutral atoms		Negative ions	
			System		System		System
$2p^1$	2P	C	0.88085	B	0.40491		
$2p^2$	3P	N	2.54998	C	1.39425	B	0.53604
	1D		2.50114		1.35552		0.49119
	1S		2.42858		1.29785		0.51252
$2p^3$	4S	O	5.21731	N	3.17939	C	1.60538
	2D		5.13555		3.11391		1.54622
	2P		5.08115		3.07051		1.50570
$2p^4$	3P	F	8.94324	O	5.84933	N	3.36944
	1D		8.88588		5.80080		3.32681
	1S		8.79700		5.72740		3.26152
$2p^5$	2P	Ne	14.06424	F	9.71118	O	6.12790
$2p^6$	1S	Na	20.78773	Ne	14.97543	F	10.08886
$3s^1$	2S	Mg	27.58848	Na	20.80104		
$3s^2$	1S	Al	35.39230	Mg	27.60894	Na	20.80392
$3p^1$	2P	Si	44.56300	Al	35.59283		
$3p^2$	3P	P	55.08558	Si	44.82954	Al	35.66672
	1D		55.06518		44.81350		35.46262
	1S		55.03452		44.78686		35.60850
$3p^3$	4S	S	67.05839	P	55.42108	Si	44.95406
	2D		67.02311		55.39441		44.93002
	2P		67.00054		55.37640		44.90803
$3p^4$	3P	Cl	80.50782	S	67.41237	P	55.55414
	1D		80.49627		67.39138		55.53360
	1S		80.44737		67.36053		55.50495
$3p^5$	2P	A	95.59085	Cl	80.94511	S	67.59899
$3p^6$	1S	K	112.3869	A	96.10217	Cl	81.18783
$4s^1$	2S	Ca	130.1744	K	112.4413		
$4s^2$	1S			Ca	130.2436	K	112.4485
$3d^1$	2D			Sc	150.6497		
$3d^2$	3F	Sc	151.4151	Ti	173.2858	Sc	151.3041
$3d^3$	4F	Ti	174.1834	V	198.1598	Ti	174.0642
$3d^4$	5D	V	199.1627	Cr	225.3846	V	199.0490
$3d^5$	6S	Cr	226.5326	Mn	255.0946	Cr	226.3239
$3d^6$	5D	Mn	256.1654	Fe	287.1840	Mn	256.0124
$3d^7$	4F	Fe	288.4189	Co	322.0240	Fe	288.2575
$3d^8$	3F	Co	323.3581	Ni	359.7512	Co	323.1725
$3d^9$	2D	Ni	360.9808	Cu	400.0073		
$3d^{10}$	1S	Cu	401.6254				
$4s^1$	2S	Zn	443.5981	Cu	401.4520	Ni	367.0901
$4s^2$	1S	Ga	487.8287	Zn	443.4911	Cu	401.4083
$4p^1$	2P	Ge	534.8446	Ga	488.0597		
$4p^2$	3P	As	584.4249	Ge	535.1090	Ga	488.1461
	1D		584.4121		535.1055		488.1216
	1S		584.3779				
$4p^3$	4S	Se	636.7640	As	584.7467	Ge	535.2614
	2D		636.6319		584.7188		535.2159
	2P		636.6039		584.7112		535.2054
$4p^4$	3P	Br	691.5456	Se	637.0015	As	584.8960
	1D		691.5312		636.9765		584.8695
	1S		691.4848		636.9552		584.8337
$4p^5$	2P	Kr	749.1885	Br	691.9457	Se	637.1991
$4p^6$	1S			Kr	749.6405	Br	692.1783

^a The positive ions of the transition elements (from Sc through Cu) have configurations $4s^0 3d^n$.

The evaluation of the interaction $\langle A \cdot A \rangle$ has been carried out using the analytical Hartree-Fock functions of Clementi [2] and Malli [9]. It has been considered more convenient to report in this case only the values of $\langle A \cdot A \rangle$, as in this way the mass polarization effect³ may then be calculated at any time for any desired isotope; the corresponding values are collected in Table 1. This contribution is more important, varying from a value of -4.40 cm^{-1} for B to a value of -1067 cm^{-1} for Kr.

The accuracy of the values for the mass polarization effect parallels the accuracy of the electronic functions used. Taking into account the characteristics ($\Delta l = \pm 1$) mentioned above, it is evident that introduction of angular correlation will affect the values. This fact is clearly evident in those systems (He, Li, Be) with s^n configurations, where the Hartree-Fock value vanishes. (Calculations have been carried out for some of these systems using correlated functions [3, 10–12].)

References

1. Bethe, H., Salpeter, E. E.: Quantum mechanics of one- and two-electron systems. New York: Academic Press 1957.
2. Clementi, E.: Tables of atomic functions. San Jose: IBM 1965.
3. Dalgarno, A., Parkinson, E. M.: Physic. Rev. **176**, 73 (1968).
4. Fraga, S., Thorhallsson, J., Fisk, C.: Canad. J. Physics **47**, 1415 (1969).
5. Innes, F. R., Ufford, C. W.: Physic. Rev. **111**, 194 (1958).
6. Lo, B. W. N., Saxena, K. M. S., Fraga, S.: Theoret. chim. Acta (Berl.) **24**, 71 (1972).
7. — — — Theoret. chim. Acta (Berl.) (in press).
8. — — — Theoret. chim. Acta (Berl.) (in press).
9. Malli, G.: Canad. J. Physics **44**, 3121 (1966).
10. Prasad, S. S., Stewart, A. L.: Proc. Physic. Soc. **87**, 159 (1966).
11. Schiff, B., Lifson, H., Pekeris, C. L., Rabinowitz, P.: Physic. Rev. **140**, A 1104 (1965).
12. Stewart, A. L.: Advanc. Physics **12**, 299 (1963).

Dr. S. Fraga
Division of Theoretical Chemistry
Department of Chemistry
University of Alberta
Edmonton 7, Alberta
Canada