Theoret. chim. Acta (Berl.) 24, 300—306 (1972)

Mass-Variation and Darwin Relativistic Corrections in Many-Electron Atoms*

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Received June 7, 1971

The formulation for the evaluation of the matrix elements over the relativisitic mass-variation and Darwin operators is presented. Calculations of these corrections have been carried out, using available analytical Hartree-Fock functions, for the positive ions, neutral systems, and negative ions for all the atoms from He to Kr.

Die Formulierung der Matrix-Elemente des Operators der relativistischen Massen-Variation und des Darwin-Operators wird angegeben. Die Größe dieser Korrekturen wird unter Benutzung bekannter analytischer Hartree-Fock-Funktionen für die positiven Ionen, neutralen Systeme und negativen Ionen aller Atome von He bis Kr berechnet.

Introduction

In order to complete the general research project under way at this Laboratory on the properties and interactions of many-electron atoms, the contributions from two terms in the Breit-Pauli hamiltonian operator are now considered: the relativistic correction to the kinetic energy due to the variation of the mass of the electrons with the velocity and the so-called Darwin correction to the potential energy, characteristic of the Dirac theory but with no classical analogue.

The calculations on two-electron systems by Pekeris and co-workers [12, 16] have shown that these terms make an appreciable contribution to the relativistic energy. Work on these operators has also been carried out by Jones [7] and Rudzikas *et al.* [14, 15], but either the two-electron part of the Darwin operator was omitted [7] or its contribution evaluated only for the electrons in the outermost shell [15].

The purpose of this work is to present a complete analysis of these operators and determine the corresponding values for the positive ions, neutral systems, and negative ions from He to Kr.

Mathematical Formulation

The Darwin and mass-variation operators are defined (in a.u.) by

$$\begin{aligned}\mathcal{H}_d &= \mathcal{H}_{d1} + \mathcal{H}_{d2} \\ &= \frac{\pi\alpha^2}{2}\left\{Z \sum_i \delta(\boldsymbol{r}_i) - 2 \sum_{i<j} \delta(\boldsymbol{r}_{ij})\right\},\end{aligned}$$

$$\mathcal{H}_p = -\frac{\alpha^2}{8} \sum_i \boldsymbol{p}_i^4 = -\frac{\alpha^2}{8} \sum_i \nabla_i^4 ,$$

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

respectively (see, e.g., Fontana and Meath [5]). Z represents the nuclear charge, $\boldsymbol{r}_i$ is the position vector of the i-th electron, associated with a linear momentum operator $\boldsymbol{p}_i$, and $\boldsymbol{r}_{ij}$ denotes the position vector of electron i relative to electron j; δ is a three-dimensional delta function and α is the fine structure constant. The summations extend over all the electrons in the system (with the restriction indicated).

The evaluation of the matrix elements of these three operators, $\mathscr{H}_{d1}$, $\mathscr{H}_{d2}$, and $\mathscr{H}_p$, is considered separately below.

One-Electron Darwin Operator

This interaction vanishes for all the orbitals with $l \neq 0$. For a single s-electron it is

$$\langle \Phi |\, \delta(\boldsymbol{r})\, | \Phi \rangle = \varrho(0)\,,$$

where $\varrho(0)$ denotes the electron density at the nucleus. The total contribution is

$$E_{d1} = \tfrac{1}{2}\pi Z \alpha^2 \sum_i n_i \varrho_i(0)\,,$$

where the summation extends over all the occupied s-orbitals in the system; n_i represents the occupation number of the i-th orbital.

Two-Electron Darwin Operator

The intershell contribution may be evaluated, through the use of generalized coefficients of fractional parentage, from the basic two-electron matrix elements (de-Shalit and Talmi [4]),

$$\begin{aligned} &\langle l_a l_b L M_L S M_S |\, \mathscr{A}^\dagger\, \hbar_{d2} \mathscr{A}\, | l_a l_b L M_L S M_S \rangle \\ &\quad = -\tfrac{1}{4}\alpha^2 [1 + (-1)^S]\,(2l_a + 1)(2l_b + 1) \begin{pmatrix} l_a & l_b & L \\ 0 & 0 & 0 \end{pmatrix}^2 R_2(a, b)\,, \end{aligned}$$

given in terms of 3-j symbols and the radial integrals $R_2(a, b)$ (that appears in the formulation for the electron spin-spin contact interaction), defined by

$$R_2(a, b) = \int_0^\infty P_a^2(r)\, P_b^2(r)\, r^{-2}\, dr\,;$$

$P(r)$ is given by $rR(r)$, where $R(r)$ is the radial function of the shell under consideration. $\hbar_{d2}$ is the two-electron Darwin operator for the two electrons involved. The general formulation may be derived following the procedure described by Lo *et al.* [8] for the electron spin-spin contact interaction.

The interaction between the electrons of a given shell, characterized by a total quantum number Γ, may be expressed as

$$\langle l_a^n \Gamma |\, \mathscr{A}^\dagger \hbar_{d2} \mathscr{A}\, | l_a^n \Gamma \rangle = -\frac{\alpha^2}{4} R_2(a, a) \sum_k (2k + 1) f_k\,,$$

where f_k are the coefficients of the Slater-Condon integrals, F^k, in the expression of the electrostatic energy of the shell considered; these values have been tabulated by Nielson and Koster [11].

On the other hand, by an argument similar to that given by Armstrong [1] for the electron spin-spin contact interaction, the intrashell contribution may be also evaluated by

$$\begin{aligned}&\langle l_a^n \Gamma | \mathscr{A}^\dagger \mathscr{h}_{d2} \mathscr{A} | l_a^n \Gamma \rangle \\ &\quad = -\frac{\alpha^2}{4} R_2(a,a) \left[(2l_a+1)(2l_a+3)^{-1} \langle e_1(l_a) \rangle + \frac{7}{6435} \langle e_2(f) \rangle \, \delta_{3,l_a} \right],\end{aligned}$$

which holds for $l_a \leqq 3$, and where $\boldsymbol{e}$ are the operators introduced by Racah [13] for the evaluation of the coulombic interactions. The matrix elements of $\boldsymbol{e}_2$ have been tabulated by Nielson and Koster [11] and the matrix elements of $\boldsymbol{e}_1$ are given by

$$\langle e_1(l) \rangle = \frac{1}{2}(2l+3)(n-v) + \frac{v}{4}(v+2) - S(S+1)$$

where v is the seniority number and S the spin quantum number of the state under consideration.

It may be observed that the intrashell interaction is equal (with sign changed) to one half of the electron spin-spin contact interaction (Fraga and Thorhallsson [6]). In fact, when the general formulation for the intershell contributions is simplified for the special case of configurations with only one open shell, one finds the same relationship between the two-electron Darwin and electron spin-spin contact contributions as for the intrashell interaction.

Mass Variation

Taking into account that

$$\nabla^2 \Phi_{nl} = \frac{\partial^2 \Phi}{\partial r^2} + \frac{2}{r} \frac{\partial \Phi}{\partial r} - \frac{l(l+1)}{r^2} \Phi,$$

one can write, for a single electron,

$$\begin{aligned}&\langle \Phi_{nl} | \boldsymbol{p}^4 | \Phi_{nl} \rangle = \langle \nabla^2 \Phi_{nl} | \nabla^2 \Phi_{nl} \rangle \\ &\quad = I_{nl}(2,2;0) - 2l(l+1)\, I_{nl}(2,0;-2) + l^2(l+1)^2\, I_{nl}(0,0;-4),\end{aligned}$$

where

$$I_{nl}(p,q;\beta) = \int_0^\infty \left(\frac{\partial^p P_{nl}}{\partial r^p} \right) r^\beta \left(\frac{\partial^q P_{nl}}{\partial r^q} \right) dr.$$

The total contribution is obtained by summation over all the occupied orbitals in the system, with consideration of the corresponding occupation numbers.

Results and Discussion

The calculations have been carried out using the analytical Hartree-Fock functions of Clementi [3] and Malli [9]; for the one-electron Darwin correction, the electronic densities at the nucleus have been taken from the work of Malli and Fraga [10].

The results for E_{d1} and E_p are presented in Tables 1 and 2, respectively; the values of E_{d2} may be obtained from those given by Lo *et al.* [8] for the electron spin-spin contact interaction.

The comparison made in Table 3 shows that, although the values of E_{d1} and E_p may be appreciable, the difference between the total contributions of the positive ion, neutral atom, and negative ion are small; in Br they are of the order of 0.2 eV. The same behavior is observed for the electron spin-spin contact interaction and consequently for E_{d2}.

Table 1. One-electron Darwin relativistic correction (in a.u.) for positive ions, neutral atoms, and negative ions

Configuration[a]	State	Positive ions		Neutral atoms		Negative ions	
		System	E_{d1}	System	E_{d1}	System	E_{d1}
$1s^2$	^1S	Li	0.00344	He	0.00060		
$2s^1$	^2S	Be	0.01180	Li	0.00347		
$2s^2$	^1S	B	0.03038	Be	0.01185	Li	0.00347
$2p^1$	^2P	C	0.06450	B	0.03008		
$2p^2$	^3P	N	0.12145	C	0.06399	B	0.02998
	^1D		0.12146		0.06398		0.03004
	^1S		0.12155		0.06405		0.03000
$2p^3$	^4S	O	0.20964	N	0.12059	C	0.06372
	^2D		0.20969		0.12069		0.06380
	^2P		0.20975		0.12076		0.06382
$2p^4$	^3P	F	0.33903	O	0.20866	N	0.12032
	^1D		0.33915		0.20871		0.12039
	^1S		0.33923		0.20874		0.12049
$2p^5$	^2P	Ne	0.52053	F	0.33765	O	0.20817
$2p^6$	^1S	Na	0.76685	Ne	0.51839	F	0.33678
$3s^1$	^2S	Mg	1.09715	Na	0.76661		
$3s^2$	^1S	Al	1.52603	Mg	1.09744	Na	0.76742
$3p^1$	^2P	Si	2.06880	Al	1.52468		
$3p^2$	^3P	P	2.74472	Si	2.06638	Al	1.52517
	^1D		2.74482		2.06653		1.52582
	^1S		2.74504		2.06667		1.52564
$3p^3$	^4S	S	3.57380	P	2.74168	Si	2.06702
	^2D		3.57293		2.74183		2.06689
	^2P		3.57494		2.74196		2.06789
$3p^4$	^3P	Cl	4.57875	S	3.57088	P	2.74210
	^1D		4.57986		3.57095		2.74203
	^1S		4.58010		3.57104		2.74262
$3p^5$	^2P	A	5.78349	Cl	4.57553	S	3.57176
$3p^6$	^1S	K	7.21205	A	5.77858	Cl	4.57672
$4s^1$	^2S	Ca	8.89708	K	7.21492		
$4s^2$	^1S			Ca	8.89869	K	7.21473
$3d^1$	^2D			Sc	10.86095		
$3d^2$	^3F	Sc	10.85295	Ti	13.12938	Sc	10.85599
$3d^3$	^4F	Ti	13.11990	V	15.73476	Ti	13.12280
$3d^4$	^5D	V	15.71815	Cr	18.71068	V	15.72703
$3d^5$	^6S	Cr	18.69686	Mn	22.08627	Cr	18.70822
$3d^6$	^5D	Mn	22.07164	Fe	25.89059	Mn	22.07664
$3d^7$	^4F	Fe	25.87280	Co	30.18592	Fe	25.87874
$3d^8$	^3F	Co	30.16532	Ni	34.98439	Co	30.17319

Table 1 (continued)

Configuration[a]	State	Positive ions		Neutral atoms		Negative ions	
		System	E_{d1}	System	E_{d1}	System	E_{d1}
$3d^9$	^2D	Ni	34.96177	Cu	40.33657		
$3d^{10}$	^1S	Cu	40.31049				
$4s^1$	^2S	Zn	46.26943	Cu	40.32028	Ni	34.96657
$4s^2$	^1S	Ga	52.85411	Zn	46.27901	Cu	40.31900
$4p^1$	^2P	Ge	60.12327	Ga	52.84791		
$4p^2$	^3P	As	68.16196	Ge	60.13149	Ga	52.84968
	^1D		68.16357		60.13261		52.85040
	^1S		68.16474				
$4p^3$	^4S	Se	76.94111	As	68.15581	Ge	60.12791
	^2D		76.94076		68.15608		60.12854
	^2P		76.94081		68.15682		60.12952
$4p^4$	^3P	Br	86.53040	Se	76.93409	As	68.15285
	^1D		86.53080		76.93328		68.15278
	^1S		86.53253		76.93528		68.15369
$4p^5$	^2P	Kr	97.00863	Br	86.52348	Se	76.92820
$4p^6$	^1S			Kr	96.99735	Br	86.51686

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

Table 2. Relativistic correction (in a.u.) due to mass variation in positive ions, neutral atoms, and negative ions[a]

Configuration[b]	State	Positive ions		Neutral atoms		Negative ions	
		System	E_p	System	E_p	System	E_p
$1s^2$	^1S	Li	0.00410	He	0.00070		
$2s^1$	^2S	Be	0.01435	Li	0.00415		
$2s^2$	^1S	B	0.03723	Be	0.01439	Li	0.00415
$2p^1$	^2P	C	0.07969	B	0.03685		
$2p^2$	^3P	N	0.15109	C	0.07901	B	0.03671
	^1D		0.15106		0.07896		0.03680
	^1S		0.15119		0.07905		0.03674
$2p^3$	^4S	O	0.26242	N	0.14989	C	0.07863
	^2D		0.26242		0.15002		0.07873
	^2P		0.26250		0.15012		0.07874
$2p^4$	^3P	F	0.42678	O	0.26106	N	0.14950
	^1D		0.42694		0.26111		0.14959
	^1S		0.42698		0.26110		0.14973
$2p^5$	^2P	Ne	0.65874	F	0.42487	O	0.26034
$2p^6$	^1S	Na	0.97561	Ne	0.65562	F	0.42353
$3s^1$	^2S	Mg	1.40313	Na	0.97486		
$3s^2$	^1S	Al	1.96106	Mg	1.40327	Na	0.97642
$3p^1$	^2P	Si	2.67085	Al	1.95905		
$3p^2$	^3P	P	3.55871	Si	2.66702	Al	1.96024
	^1D		3.55882		2.66722		1.96144
	^1S		3.55897		2.66740		1.96090
$3p^3$	^4S	S	4.65181	P	3.55385	Si	2.66882
	^2D		4.65007		3.55400		2.66836
	^2P		4.65377		3.55417		2.67028
$3p^4$	^3P	Cl	5.98218	S	4.64733	P	3.55507
	^1D		5.98399		4.64740		3.55482

Table 2 (continued)

Configuration[b]	State	Positive ions System	Positive ions E_p	Neutral atoms System	Neutral atoms E_p	Negative ions System	Negative ions E_p
	^1S		5.98452		4.64743		3.55589
$3p^5$	^2P	A	7.58411	Cl	5.97771	S	4.64980
$3p^6$	^1S	K	9.49112	A	7.57683	Cl	5.98106
$4s^1$	^2S	Ca	11.74674	K	9.49617		
$4s^2$	^1S			Ca	11.74907	K	9.49595
$3d^1$	^2D			Sc	14.38126		
$3d^2$	^3F	Sc	14.36690	Ti	17.42976	Sc	14.37187
$3d^3$	^4F	Ti	17.41318	V	20.93745	Ti	17.41748
$3d^4$	^5D	V	20.90692	Cr	24.95282	V	20.92319
$3d^5$	^6S	Cr	24.92782	Mn	29.51192	Cr	24.94469
$3d^6$	^5D	Mn	29.48658	Fe	34.65538	Mn	29.49414
$3d^7$	^4F	Fe	34.62364	Co	40.48981	Fe	34.63348
$3d^8$	^3F	Co	40.45271	Ni	47.00052	Co	40.46618
$3d^9$	^2D	Ni	46.95903	Cu	54.28218		
$3d^{10}$	^1S	Cu	54.23631				
$4s^1$	^2S	Zn	62.36221	Cu	54.25142	Ni	46.97402
$4s^2$	^1S	Ga	71.34233	Zn	62.37778	Cu	54.24996
$4p^1$	^2P	Ge	81.30165	Ga	71.33870		
$4p^2$	^3P	As	92.34089	Ge	81.31519	Ga	71.34369
	^1D		92.34299		81.31675		71.34452
	^1S		92.34405				
$4p^3$	^4S	Se	104.4074	As	92.33386	Ge	81.31022
	^2D		104.4066		92.33448		81.31091
	^2P		104.4066		92.33467		81.31230
$4p^4$	^3P	Br	117.6005	Se	104.3989	As	92.32967
	^1D		117.6009		104.3977		92.32947
	^1S		117.6025		104.4003		92.33064
$4p^5$	^2P	Kr	132.0507	Br	117.5924	Se	104.3912
$4p^6$	^1S			Kr	132.0373	Br	117.5838

[a] All the values in this Table are negative.

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

Table 3. Comparison of the orbital contributions to the relativistic corrections (in a.u.) in Br and its ions

	Correction for mass variation[a]			One-electron Darwin correction		
	$Br^+(^3P)$	$Br(^2P)$	$Br^-(^1S)$	$Br^+(^3P)$	$Br(^2P)$	$Br^-(^1S)$
1s	96.34546	96.34724	96.34673	77.56520	77.56668	77.56619
2s	12.07728	12.07627	12.07606	7.63681	7.63619	7.63603
3s	2.004271	2.00354	2.00313	1.20753	1.20709	1.20684
4s	0.20268	0.19035	0.18076	0.12086	0.11351	0.10780
2p	5.57172	5.57144	5.57156			
3p	1.03087	1.03083	1.03157			
4p	0.05414	0.05896	0.06031			
3d	0.31411	0.31379	0.31372			
Total	117.6005	117.5924	117.5838	86.53040	86.52348	86.51686
|Difference|		0.00860	0.00810		0.00692	0.00662

[a] In absolute value.

Table 4. Comparison of the relativistic corrections (in cm^{-1}) evaluated for He from various functions

Correction	Function				
	Hydrogenic[a]	Hartree[a]	Hartree-Fock[b]	Hylleraas[a]	Exact[c]
E_p	−118.45	−153.28	−154.31	−159.24	−158.03
E_{d1}	112.31	132.06	132.04	133.40	132.94
E_{d2}	− 7.02	− 6.90	− 7.00	− 8.30	− 3.91
Sum	− 13.16	− 28.11	− 29.27	− 34.14	− 29.00

[a] Evaluated by Sessler and Foley [17] and Bethe and Salpeter [2].
[b] This work.
[c] As given by Stewart [18] and Bethe and Salpeter [2].

A more detailed study of these interactions is made in Table 4 for He, where results obtained from different functions are available. In this connection it must be mentioned that all the values quoted from the work of Sessler and Foley [17] for E_{d2} have been multiplied by 2, as the operator used in their work is affected by a factor $\frac{1}{2}$, by comparison to the expressions usually accepted (see e.g., Fontana and Meath [5], Rudzikas [14], and Stewart [18]). The discrepancy observed for the value of E_{d2} obtained from the Hylleraas function cannot be explained; it should be similar to that obtained for the Pekeris function. In any case it may be concluded that Hartree-Fock functions provide a satisfactory description of these interactions in many-electron atoms.

References

1. Armstrong, L., Jr.: Physic. Rev. **170**, 122 (1968).
2. Bethe, H. A., Salpeter, E. E.: Quantum mechanics of one- and two-electron atoms. New York: Academic Press 1957.
3. Clementi, E.: Tables of atomic functions. San Jose: IBM 1965.
4. De-Shalit, A., Talmi, I.: Nuclear shell theory. New York: Academic Press 1963.
5. Fontana, P. R., Meath, W. J.: J. math. Physics **9**, 1357 (1968).
6. Fraga, S., Thorhallsson, J.: Physic. Rev. **178**, 70 (1969).
7. Jones, M.: J. Physics B **3**, 1571 (1970).
8. Lo, B. W. N., Saxena, K. M. S., Fraga, S.: Theoret. chim. Acta (Berl.) (in press).
9. Malli, G.: Canad. J. Physics **44**, 3121 (1966).
10. —, Fraga, S.: Canad. J. Physics **44**, 3131 (1966).
11. Nielson, C. W., Koster, G. F.: Spectroscopic coefficients for the p^n, d^n and f^n configurations. Cambridge: MIT Press 1963.
12. Pekeris, C. L.: Physic. Rev. **112**, 1649 (1958).
13. Racah, G.: Physic. Rev. **76**, 1352 (1949).
14. Rudzikas, Z.: Liet. Fiz. Rinkinys **9**, 707 (1969).
15. —, Karaziya, R.: Liet. Fiz. Rinkinys **10**, 13 (1970).
16. Schiff, B., Lifson, H., Pekeris, C. L., Rabinowitz, P.: Physic. Rev. **140**, A 1104 (1965).
17. Sessler, A. M., Foley, H. M.: Physic. Rev. **92**, 1321 (1953).
18. Stewart, A. L.: Advan. Physics **12**, 299 (1963).

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