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Physical Properties of Many-Electron Atomic Systems Evaluated from Analytical Hartree-Fock Functions

VIII. The Use of Approximate Functions for Lowest and Excited States*

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Two types of approximate functions have been tested through the evaluation of various physical properties: for ground states, double-ζ, SCF functions have been used, while for excited states the calculations have been carried out using the expectation values obtained from the Hartree-Fock functions for the corresponding lowest configuration. The agreement with the Hartree-Fock values or the experimental results, respectively, can be considered to be very satisfactory.

Introduction

The *a priori* calculation of physical properties and interactions implies the availability of accurate functions. For many-electron atoms, analytical Hartree-Fock functions are available for the states arising from the lowest electronic configurations of neutral systems, positive and negative ions, and for various isoelectronic series.

These functions have been used in a comprehensive study of various properties and interactions, namely: dipole polarizabilities [19], nuclear magnetic shielding constants [9], diamagnetic susceptibilities [10], electric field gradients and quadrupole coupling constants [11], magnetic hyperfine structure constants [14], Fermi contact interaction [12], octopole coupling constants [13], orbit-orbit-interactions [6, 20], spin-orbit coupling constants [5, 15, 16, 18], and spin-spin coupling constants [21].

The purpose of this work is to investigate the possible use of approximate functions for the evaluation of the properties mentioned above for both lowest and excited states, either as a test of the accuracy of the function involved or as an approximation to the exact value of the corresponding property, as discussed below.

That is, in the case of lowest states there is, of course, no need of using such approximate functions, as the corresponding Hartree-Fock functions are available. It could be interesting, however, to see that simpler functions provide an overall description very similar to that given by the Hartree-Fock functions. Such functions could then be used in simple molecular calculations, in the hope of obtaining satisfactory results without having to make use of the longer expansions of the Hartree-Fock orbitals.

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The situation regarding excited states is different in that very few accurate functions are available. In such a case the interest of the present calculations centers on the results obtained for the properties.

Description of the Approximate Functions

For the lowest states, the functions used are the so-called double-ζ, SCF functions, determined by Clementi [2].

Regarding the excited states, the situation is as follows. Bagus [1] carried out calculations for a number of Ne- and Ar-like systems, determining the Hartree-Fock functions for the lowest as well as for the various excited states resulting from the excitation of a single electron from the inner shells to the highest open shell. The properties evaluated from these functions present certain regularities, as observed by Valdemoro and Fraga [22].

A detailed compilation of expectation values and other quantities, using the Hartree-Fock functions of Bagus [1], has now been made[1]. It can be observed that the values seem to be invariant with respect to excitations within the highest open shell: for example, the values are essentially identical for the two configurations $K(2)\,L(8)\,3s^2\,3p^5$ and $K(2)\,L(8)\,3s^1\,3p^6$ of Cl, and similarly for the other systems.

On the basis of this numerical evidence, one is led to assume that this behavior may be general. Consequently, calculations of properties and interactions, carried out by using the expectation values obtained from the Hartree-Fock functions for the lowest states, should lead to values with an accuracy of the same order as that obtained for the lowest states.

Details of the Calculations

In this work, most of the properties and interactions mentioned above have been calculated for the ground states of He to Ar, using the double-ζ, SCF functions of Clementi [2], and for some exited configurations of the atoms He to Kr, using the values obtained from the Hartree-Fock functions of Clementi [2] and Malli [8] for the corresponding lowest configurations. Only the results[2] for spin-orbit coupling constants are discussed here.

For the lowest states of the electronic configurations under consideration, the spin-orbit coupling constants have been determined from the expressions

$$\lambda(s^1p^n, S, L) = [(S-\tfrac{1}{2})/S]\,\lambda(p^n, S-\tfrac{1}{2}, L)\,,$$

$$\lambda(s^1d^n, S, L) = [(S-\tfrac{1}{2})/S]\,\lambda(d^n, S-\tfrac{1}{2}, L)\,,$$

$$\lambda(p^5d^n, S, L) = (1/2SL)\,\lambda(p^5, {}^2P) + [(S-\tfrac{1}{2})\,(L-1)/SL]\,\lambda(d^n, S-\tfrac{1}{2}, L-1)\,,$$

derived from the formulation of Goudsmit and Humphreys [7], Condon and Shortley [3], and Edlen [4].

In these expressions, the coupling constants $\lambda(l^n, S, L)$ are defined by

$$\lambda(l^n, S, L) = \zeta_l\,\eta(l^n, S, L)\,,$$

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[1] These results have been collected in the Technical Report TC-6805, Department of Chemistry, University of Alberta. A limited number of copies are available from the authors upon request.

[2] The complete results have been included in the Technical Report TC-6805, mentioned above.

where ζ_l denotes the individual splitting factor

$$\zeta_l = (\alpha^2/2) \left\{ Z\langle r_l^{-3}\rangle - \sum_i \int_0^\infty (1/r^3)\, R_l^2(r)\, r^2\, dr \int_0^r R_{l_i}^2(r_i)\, r_i^2\, dr_i \right\},$$

of the open shell under consideration. In this expression α is the fine structure constant, Z is the nuclear charge, and R_l represents the radial function of the orbital with angular momentum quantum number l. The summation extends over all the electrons in the inner shells and the other electrons, if any, in the open shell.

Taking into account that the correction terms corresponding to an excitation of the type considered here are negligible (at least for the systems considered here), the individual splitting factors obtained from the lowest states have been used in the present calculations. In addition, in those cases in which the correction terms had not been calculated for the lowest state (e.g., when the open shell in the lowest state was a half-filled shell, in which case there is no spin-orbit coupling), they have been determined by a simple interpolation.

The values given by Malli and Fraga [15] for the parameters $\eta(l^n, S, L)$ have been used in these calculations.

Results and Discussion

The results of these calculations are presented in Tabs. 1 and 2, for the different types of configurations considered here.

In Table 1, comparison is made with the spin-orbit coupling constant, λ, determined from the experimental data of Moore [17] by means of the relation

$$E(J) - E(J-1) = \lambda J\,,$$

where J denotes the total electronic angular momentum quantum number. It can be observed that the agreement between the theoretical and experimental values is of the same order as for the lowest state, especially for the heavy elements.

It could be concluded therefore that the results obtained for the remaining properties are just as satisfactory.

In addition, it must be mentioned that the results obtained from the double-ζ, SCF functions are in excellent agreement with the values calculated from the Hartree-Fock functions.

Table 1. *Absolute values*[a] *of spin-orbit coupling constants λ (in cm^{-1}) for some excited states of positive ions, neutral atoms, and negative ions with s^1p^n configurations*[b] *(experimental values in parentheses)*

Configuration[b]	State	Positive ions			Neutral atoms			Negative ions	
$2s^12p^2$	^4P	C^+	19.29	(13.0)	B	5.11	(2.9)		
$2s^12p^4$	^4P	O^+	74.13	(60.1)	N	32.52	(15.3)	C^-	10.54
$2s^12p^5$	^3P	F^+	187.76	(164.3)	O	90.74	(40.1)	N^-	36.21
$3s^13p^2$	^4P	Si^+	61.27	(71.6)	Al	22.78	(30.7)		
$3s^13p^4$	^4P	S^+	156.32	(142.6)	P	83.06	(71.0)	Si^-	35.78
$3s^13p^5$	^3P	Cl^+	338.26	(325.1)	S	195.28		P^-	97.07
$4s^14p^2$	^4P	Ge^+	349.99	(453.6)	Ga	159.71	(237.0)		
$4s^14p^4$	^4P	Se^+	673.83	(626.6)	As	413.44	(507.6)	Ge^-	203.50
$4s^14p^5$	^3P	Br^+	1303.68	(1184.0)	Se	852.37		As^-	485.46

[a] For $n > 3$, the values are negative.

[b] The complete configurations are $K(2)2s(1)3p(n)$, $K(2)L(8)3s(1)3p(n)$, and $K(2)L(8)M(18)4s(1)\cdot 4p(n)$, respectively.

Table 2. *Spin-orbit coupling constants* λ *(in* cm^{-1}*) for some excited states of positive ions, neutral atoms, and negative ions with* s^1d^n *and* p^5d^n *configurations*

Configuration	State	Positive ion[a]		Neutral atom[b]		Negative ion[b]	
$3s^13d^2$	^4F			Sc	31.99		
$3s^13d^3$	^5F	Sc$^+$	19.63	Ti	37.05	Sc$^-$	17.39
$3s^13d^4$	^6D	Ti$^+$	24.90	V	42.07	Ti$^-$	23.51
$3s^13d^6$	^6D	Cr$^+$	−50.67	Mn	−75.74	Cr$^-$	−49.42
$3s^13d^7$	^5F	Mn$^+$	−83.00	Fe	−120.17	Mn$^-$	−81.54
$3s^13d^8$	^4F	Fe$^+$	−143.52	Co	−201.72	Fe$^-$	−141.53
$3s^13d^9$	^3D	Co$^+$	−273.86	Ni	−375.69	Co$^-$	−271.44
Configuration	State	Positive ion[c]		Neutral atom[d]		Negative ion[d]	
$3p^53d^2$	^4G			Sc	−205.31		
$3p^53d^3$	^5G	Sc$^+$	−152.01	Ti	−193.97	Sc$^-$	−154.60
$3p^53d^4$	^6F	Ti$^+$	−213.79	V	−270.88	Ti$^-$	−215.19
$3p^53d^5$	^7P	V$^+$	−729.24	Cr	−930.77	V$^-$	−730.85
$3p^53d^6$	^6F	Cr$^+$	−396.16	Mn	−503.34	Cr$^-$	−396.88
$3p^53d^7$	^5G	Mn$^+$	−479.26	Fe	−606.91	Mn$^-$	−478.94
$3p^53d^8$	^4G	Fe$^+$	−784.27	Co	−981.86	Fe$^-$	−784.23
$3p^53d^9$	^3F	Co$^+$	−1815.69	Ni	−2234.49	Co$^-$	−1817.19
$3p^53d^{10}$	^2P	Ni$^+$	−11687.67	Cu	−14075.66		

[a] The complete configuration is $K(2)L(8)3s(1)3p(6)3d(n)$.

[b] The complete configuration is $K(2)L(8)3s(1)3p(6)3d(n)4s(2)$.

[c] The complete configuration is $K(2)L(8)3s(2)3p(5)3d(n)$.

[d] The complete configuration is $K(2)L(8)3s(2)3p(5)3d(n)4s(2)$.

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