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

VII. Electric Dipole Polarizabilities*

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The electric dipole polarizabilities have been evaluated from Hartree-Fock functions for the positive ions, neutral atoms, and negative ions from He to Kr. The agreement with previous theoretical results and with experimental values, whenever available, is rather satisfactory. On the basis of this agreement, the simple method used appears to be competitive with more elaborate treatments.

Die Polarisierbarkeit der Atome und der positiven und negativen Ionen von He bis Kr ist nach einem verhältnismäßig einfachen Verfahren mit Hartree-Fock-Funktionen berechnet worden. Die Ergebnisse stimmen recht gut mit schon vorhandenen theoretischen und experimentellen Ergebnissen überein.

On a calculé les polarisabilités dipolaires pour tous les ions positifs, les atomes neutres et les ions négatifs jusqu'au Krypton en employant des fonctions analytiques de Hartree-Fock. L'accord avec autres résultats théoriques et les valeurs expérimentales est satisfaissant. La simple méthode employée ici offre donc une alternative en comparison avec des méthodes plus élaborées.

Introduction

In the preceding papers of this series [21–26] the values of various physical properties[1], calculated from analytical Hartree-Fock functions, have been reported for the positive ions, neutral atoms, and negative ions from He to Kr. Dipole polarizabilities have now been calculated for these systems.

It must be mentioned that for some of these systems, polarizabilities have been calculated by a number of researchers (see Tabs. 1 and 2). The present work, however, provides a comprehensive set of results for all these systems and shows the usefulness of a rather simple method in predicting quite satisfactory values.

Theoretical Considerations

When an atom is placed in an uniform electric field, F, a dipole moment is induced. This moment is proportional to the field, the constant of proportionality (α) being the so-called atomic dipole polarizability.

Perturbation theory can be used, in principle, for the evaluation of the dipole polarizability, but the difficulties encountered in its practical application render the problem untractable. There is, however, an alternate treatment based on perturbation theory and involving a variational procedure.

When considering a weak field, the perturbed function Φ may be approximated as [13]

$$\Phi = \Phi_0(1 + \omega),$$

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[1] Additional results have been presented elsewhere [11, 12, 36, 37].

where Φ_0 represents the unperturbed function and ω denotes a symmetric function, to be determined by a variational treatment.

Several treatments, differing in the form adopted for the function ω, have been formulated. Kirkwood [18] used the function

$$\omega = \mu \sum_i v(r_i),$$

where $v(r_i)$ represents the potential due to the field at the position of the i-th electron and the summation extends over all the electrons in the system.

A more complete treatment was carried out by Pople and Schofield [29], using a function

$$\omega = \sum_i u(r_i),$$

where the summation extends also over all the electrons. The function $u(r_i)$ is the solution of a second order differential equation, for which Pople and Schofield [29] used numerical integration.

A simpler formulation, leading to satisfactory results, can however be used. For Argon, Pople and Schofield [29] showed that the relation

$$u(r) = F(\mu r + \nu r^2)\cos\theta$$

holds approximately. This relation has been adopted in the present work.

In such a case, the energy in the presence of a weak field is given by

$$E = E_0 + \tfrac{1}{2}[A_0\mu^2 + 2A_2\nu^2 + \tfrac{4}{3}(B_0\mu + 2A_1\mu\nu + B_1\nu)]\,F^2\,, \tag{1}$$

where E_0 denotes the unperturbed energy and A_k, B_k are given by

$$A_k = \langle \Phi_0 | \sum_i r_i^k | \Phi_0 \rangle\,,$$

$$B_k = \langle \Phi_0 | \sum_{i,j} r_i^k (r_i \cdot r_j) | \Phi_0 \rangle\,,$$

respectively. Minimization of the energy with respect to μ and ν leads to the relations

$$\mu = (4A_1B_1 - 6A_2B_0)/(9A_0A_2 - 8A_1^2)\,,$$

$$\nu = (4A_1B_0 - 3A_0B_1)/(9A_0A_2 - 8A_1^2)\,.$$

The dipole polarizability can be evaluated now taking into account that the energy is also given by

$$E = E_0 - \tfrac{1}{2}\alpha F^2\,. \tag{2}$$

Comparison of Eqs. (1) and (2) leads to

$$\alpha = -[A_0\mu^2 + 2A_2\nu^2 + \tfrac{4}{3}(B_0\mu + 2A_1\mu\nu + B_1\nu)]\,. \tag{3}$$

Results and Discussion

The evaluation of the dipole polarizability by means of Eq. (3) can be carried out if the unperturbed function Φ_0, needed for the evaluation of the parameters A_k, B_k, is known. In the present work, the analytical Hartree-Fock functions of Clementi [4], Malli [20], Roothaan and Synek [30], and Synek and Stungis [31] have been used.

The corresponding results are presented in Tab. 1 and 2, and compared with other theoretical results and with experimental values, whenever available. In particular, Tab. 1 shows that for the rare gases the agreement with the experimental

Table 1. *Dipole polarizabilities (in Å^3) for the ground states of some rare gases*

System	This work[a]	This work[b]	Sternheimer method[c]	Hartree-Fock[c, d]	Experimental[c]
He	0.220	0.185	0.220 [8]	0.196 [5]	0.2068 [15]
Ne	0.395	0.579	0.38 [10]	0.409 [38]	0.398 [19]
Ar[e]	1.99	2.48	2.40 [16]	2.32 [38]	1.63 [19]
Kr	3.12	2.86			2.48 [6]
Xe	3.27	3.91			4.01 [19]

[a] Values calculated from the Hartree-Fock functions of Clementi [4], Malli [20], and Synek and Stungis [31], using the formulation discussed in this work.

[b] Values calculated in this work from the same functions mentioned above, using the formulation of Kirkwood [18].

[c] Values taken from the literature. The corresponding references are given next to the values.

[d] These values were obtained by a coupled or uncoupled Hartree-Fock procedure.

[e] Pople and Schofield [29] calculated a value of 2.03 Å^3.

Table 2. *Dipole polarizabilities (in Å^3) for various states of neutral atoms and positive and negative ions*[a]

System	Positive ion			Neutral atom			Negative ion		
	State	α	Ref.	State	α	Ref.	State	α	Ref.
Li	^{1}S	0.030		^{2}S	16.0		^{1}S	269	
		(0.0304)	[8]		(20.0)	[35]			
		[0.0280]	[5]		[21.0]	[38]			
		0.0235	[32]		*22±2*	[3]			
Be	^{2}S	1.82		^{1}S	7.77				
		[2.48]	[38]		(9.5)	[9]			
					[6.76]	[7]			
					6.93[b]				
B	^{1}S	1.54		^{2}P	3.43		^{3}P	28.2	
		[1.68]	[5]		(5.1)	[10]			
C	^{2}P	0.819		^{3}P	1.75		^{4}S	7.37	
					(2.1)	[10]			
N	^{3}P	0.497		^{4}S	1.04		^{3}P	4.73	
					(1.3)	[10]			
O	^{4}S	0.329		^{3}P	0.732		^{2}P	2.85	
		(0.49)	[28]		(0.89)	[10]		(3.2)	[28]
F	^{3}P	0.253		^{2}P	0.535		^{1}S	1.71	
					(0.6)	[10]		(1.8)	[10]
								[1.81]	[38]
								0.99	[2]
Na	^{1}S	0.155		^{2}S	18.6		^{1}S	250	
		(0.152)	[33]		(22.9)	[34]			
		[0.163]	[38]		[27.1]	[38]			
		0.17	[27]		*21.5±2*	[3]			
Mg	^{2}S	3.49		^{1}S	14.1				
		[5.51]	[38]		[19.4]	[38]			
					7.0±1.8	[1]			
					7.4±1.8	[1]			
Al	^{1}S	4.02		^{2}P	11.0		^{3}P	74.6	
		[5.89]	[38]						

Table 2 (continued)

System	Positive ion			Neutral atom			Negative ion		
	State	α	Ref	State	α	Ref.	State	α	Ref.
Si	^2P	3.18		^3P	6.81		^4S	22.4	
P	^3P	2.37		^4S	4.42		^3P	14.7	
S	^4S	1.77		^3P	3.45		^2P	9.11	
Cl	^3P	1.46		^2P	2.61		^1S	5.89	
								(7.19)	[33]
								[6.23]	[38]
								3.05	[2]
K	^1S	0.944		^2S	37.3		^1S	568	
		(1.24)	[33]		(44.4)	[34]			
		[1.08]	[38]		[59.6]	[38]			
		0.80	[27]		*45.7 ± 6*	[14]			
Ca	^2S	8.34		^1S	33.8				
		[14.3]	[38]		[48.9]	[38]			
					19.7 ± 0.6	[1]			
					22.5 ± 0.6	[1]			
Sc	^3F	2.06		^2D	26.8		^3F	197	
Ti	^4F	1.67		^3F	22.4		^4F	204	
V	^5D	1.41		^4F	19.1		^5D	189	
Cr	^6S	1.16		^5D	16.6		^6S	175	
Mn	^5D	1.13		^6S	14.6		^5D	146	
Fe	^4F	1.03		^5D	12.7		^4F	134	
Co	^3F	0.896		^4F	11.3		^3F	114	
Ni	^2D	0.845		^3F	10.2		^2S	35.4	
Cu	^1S	0.742		^2S	9.10		^1S	92.8	
		(0.982)	[33]						
Zn	^2S	2.22		^1S	8.12				
Ga	^1S	3.01		^2P	9.31		^3P	81.8	
Ge	^2P	3.11		^3P	6.97		^4S	23.4	
As	^3P	2.73		^4S	5.22		^3P	17.0	
Se	^4S	2.32		^3P	4.50		^2P	11.9	
Br	^3P	2.13		^2P	3.79		^1S	8.18	
Mo				^7S	13.4				

[a] The first value given for each system represents the dipole polarizability calculated in the present work from the Hartree-Fock functions of Clementi [4], Malli [20] and Roothaan and Synek [30]. The values in parentheses are those obtained by the Sternheimer method, while the values in brackets have been obtained by a Hartree-Fock formulation. The experimental values, whenever available, are given in italic. For all the values taken from the literature, the corresponding references are given next to them.

[b] Value determined by Kelly [17] in an exact calculation.

values is excellent up to Argon. As a matter of fact, the present results are even better than those obtained by more elaborate treatments.

For the neutral atoms the agreement with the experimental values worsens with increasing atomic number, as expected. For positive ions the agreement can be considered to be reasonably good, while it is rather poor for the negative ions.

Taking into account that the results from other treatments offer a similar behavior, one would be inclined to ascribe the disagreement rather to the unperturbed function than to the method used. That is, the expression for the dipole polarizability involves the parameters A_2 and B_1, for which the main contributions come from the outer regions of the electronic charge distribution. The deviation from the exact distribution in such a region may be appreciable for Hartree-Fock functions in the case of negative ions.

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