

On the Hyperpolarizability of the Lithium Dimer

George Maroulis

Laboratoire de Chimie Quantique, Université Catholique de Louvain, Pl. L. Pasteur 1,
1348 Louvain-La-Neuve, Belgium

Z. Naturforsch. **41a**, 756–760 (1986); received December 24, 1985

All independent components of all electric polarizability and hyperpolarizability tensors up to the fourth rank have been calculated near the Hartree-Fock limit for $\text{Li}_2(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2, X^1\Sigma_g^+)$. Many of the molecular properties reported in this paper appear for the first time in the literature. Our values for the isotropic components of the C , B and γ hyperpolarizabilities are $1487\text{ e}^2 a_0^4 E_h^{-1}$, $-490 \times 10^2\text{ e}^3 a_0^4 E_h^{-2}$ and $510.5 \times 10^3\text{ e}^4 a_0^4 E_h^{-3}$ respectively.

I. Introduction and Theory

The importance of electric moments and polarizabilities in the interpretation of a large variety of phenomena has increased considerably the interest in both accurate predictions and experimental determinations of these properties [1]. Among the most important theoretical contributions to the field we note the calculation of dipole moments and static electric dipole polarizabilities for Ne, HF, H_2O , NH_3 , CH_4 and CO from both SCF and correlated wavefunctions by Werner and Meyer [2], the Many-Body-Perturbation-Theory (MBPT) treatment of electron correlation effects on the dipole polarizabilities and hyperpolarizabilities of FH reported by Bartlett and Purvis [2], the Variation-Perturbation Theoretic (VPT) calculation of all polarizability tensors up to the fourth rank for H_2^+ by Bishop and Cheung [2], the Coupled Hartree-Fock (CHF) calculation of the first dipole hyperpolarizability for H_2O , NH_3 , CH_4 and CO by Lazzeretti and Zanassi [2], the SCF study of the NeHF van der Waals molecule by Fowler and Buckingham [2], the elegant reformulation of the theory of multipole moments and static polarizabilities by Applequist [2], the calculation of higher order electric moments for FH, CO and N_2 by Bounds and Wilson [2], the near Hartree-Fock calculation of electric polarizability tensors up to the sixth rank for CH_4 by Dierksen and Sadlej [2], and the application of derivative Hartree-Fock (DHF) theory to the calculation of dipole and quadrupole polarizabilities for H_2 , N_2 and acetylene by Dykstra [2]. Among the

latest contributions to the experimental determination of molecular hyperpolarizabilities we note the third harmonic generation (THG) measurements of the third-order nonlinear susceptibility of liquids by Meredith et al. [3], the four wave mixing (FWM) non-resonant third-order susceptibilities for gases reported by Lundeen et al. [3], and the measurement of second- and third-order electric polarizabilities using dc electric-field-induced second-harmonic generation by Dudley II and Ward [3].

Recently, we have reported near Hartree-Fock values for all the independent components of all electric moments and static electric polarizability tensors up to the fourth rank for the ground state of Ne [4], FH [5], BH and CH^+ [6], Be, B^+ and C^{2+} [7], Ar [8], OH^- , F^- , NeH^+ and Mg^{2+} [9], Li^+ , Li and Li^- [10], LiH [11], N_2 [12], and H_2 [13]. In this approach the electric polarizabilities and hyperpolarizabilities are calculated from the perturbed energy and multipole moments of the system in the presence of the static field of a distant electric charge. In the case of the molecular systems the calculation of the above properties for three or four different bond lengths leads to the study of their dependence on the molecular geometry. Our approach has two distinct advantages: first, a few calculations on the atom-charge or molecule-charge system suffice for the determination of all the aforementioned properties and second, no modification of the standard SCF programmes is required.

In this paper we report near Hartree-Fock values for the electric moments and static electric polarizabilities of $\text{Li}_2(1\sigma_g^2 1\sigma_u^2 2\sigma_g^2, X^1\Sigma_g^+)$ calculated from LCAO-SCF wavefunctions in the Born-Oppenheimer approximation. The theoretical study of metal clusters has attracted particular attention in recent

Reprint requests to Dr. George Maroulis, Ploutonos 44,
18121 Korydallos, Greece.

0340-4811 / 86 / 0500-0756 \$ 01.30/0. – Please order a reprint rather than making your own copy.



Dieses Werk wurde im Jahr 2013 vom Verlag Zeitschrift für Naturforschung in Zusammenarbeit mit der Max-Planck-Gesellschaft zur Förderung der Wissenschaften e.V. digitalisiert und unter folgender Lizenz veröffentlicht: Creative Commons Namensnennung-Keine Bearbeitung 3.0 Deutschland Lizenz.

Zum 01.01.2015 ist eine Anpassung der Lizenzbedingungen (Entfall der Creative Commons Lizenzbedingung „Keine Bearbeitung“) beabsichtigt, um eine Nachnutzung auch im Rahmen zukünftiger wissenschaftlicher Nutzungsformen zu ermöglichen.

This work has been digitalized and published in 2013 by Verlag Zeitschrift für Naturforschung in cooperation with the Max Planck Society for the Advancement of Science under a Creative Commons Attribution-NoDerivs 3.0 Germany License.

On 01.01.2015 it is planned to change the License Conditions (the removal of the Creative Commons License condition "no derivative works"). This is to allow reuse in the area of future scientific usage.

years [14]. Ab initio calculations on small lithium clusters have been reported at both the SCF and CI level [15]. Although previous work concerned mostly energies and molecular geometries, recent efforts focussed on the calculation of electric properties [16]. Our calculation of electric properties for Li_2 is the first complete one, in the sense that all electric moment and static polarizability tensors up to the fourth rank are included in the present study. We also report a calculation of the $\text{Li}_2\text{-e}^-$ static interaction potential and discuss the relative importance of the higher polarizabilities in intermolecular interaction studies as the magnitude of these properties leads to valuable deductions about the chemical behaviour of the molecule [17].

In this paper we follow the spirit, if not the letter, of Buckingham's paradigm and write the energy, dipole, quadrupole and octopole moments of an unchanged system in the presence of a general electric field as

$$\begin{aligned} E = E^0 &- \mu_\alpha^0 F_\alpha - \frac{1}{3} \Theta_{\alpha\beta}^0 F_\alpha F_\beta - \frac{1}{15} \Omega_{\alpha\beta\gamma}^0 F_\alpha F_\beta F_\gamma \\ &- \frac{1}{105} \Phi_{\alpha\beta\gamma\delta}^0 F_\alpha F_\beta F_\gamma F_\delta + \dots \\ &- \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{3} A_{\alpha,\beta\gamma} F_\alpha F_\beta F_\gamma \\ &- \frac{1}{6} C_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta - \frac{1}{15} E_{\alpha,\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots \\ &- \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{6} B_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots \\ &- \frac{1}{24} \gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots, \end{aligned} \quad (1)$$

$$\begin{aligned} \mu_\alpha = \mu_\alpha^0 &+ \alpha_{\alpha\beta} F_\beta + \frac{1}{3} A_{\alpha,\beta\gamma} F_\beta F_\gamma + \frac{1}{15} E_{\alpha,\beta\gamma\delta} F_\beta F_\gamma F_\delta \\ &+ \frac{1}{2} \beta_{\alpha\beta\gamma} F_\beta F_\gamma + \frac{1}{3} B_{\alpha\beta,\gamma\delta} F_\beta F_\gamma F_\delta \\ &+ \frac{1}{6} \gamma_{\alpha\beta\gamma\delta} F_\beta F_\gamma F_\delta + \dots, \end{aligned} \quad (2)$$

$$\begin{aligned} \Theta_{\alpha\beta} = \Theta_{\alpha\beta}^0 &+ A_{\gamma,\alpha\beta} F_\gamma + C_{\alpha\beta,\gamma\delta} F_\gamma F_\delta \\ &+ \frac{1}{2} B_{\gamma\delta,\alpha\beta} F_\gamma F_\delta + \dots, \end{aligned} \quad (3)$$

$$\Omega_{\alpha\beta\gamma} = \Omega_{\alpha\beta\gamma}^0 + E_{\delta,\alpha\beta\gamma} F_\delta + \dots, \quad (4)$$

where E^0 , μ^0 , Θ^0 , Ω^0 and Φ^0 are the energy and permanent multipole moments of the free molecule and α , β , γ , A , C , E and B the static electric polarizabilities. F_α , $F_{\alpha\beta}$, etc. are the electric field, field gradient etc. at the origin. The greek subscripts denote cartesian tensor components; a repeated subscript denotes a summation over all cartesian coordinates x , y and z .

For a centrosymmetric diatomic molecule, with the inversion centre as the origin, we have

$$\mu_\alpha^0 = \Omega_{\alpha\beta\gamma}^0 = \beta_{\alpha\beta\gamma} = A_{\alpha,\beta\gamma} = 0. \quad (5)$$

With z as the molecular axis, we specify the quadrupole and hexadecapole moments by their Θ_{zz} and Φ_{zzzz} components, the dipole polarizability by α_{zz} and α_{xx} , the second dipole hyperpolarizability by γ_{zzzz} , γ_{xxzz} and γ_{xxxx} , the quadrupole-quadrupole one by $C_{zz,zz}$, $C_{xz,xz}$ and $C_{xx,xx}$, the dipole-octopole by $E_{z,zzz}$ and $E_{x,xxx}$, and the dipole-dipole-quadrupole by $B_{zz,zz}$, $B_{xz,xz}$, $B_{xx,zz}$ and $B_{xx,xx}$. Relevant algebraic formulae for the computation of the above tensor components were given in previous papers [4–13]. In this work we follow a similar but slightly different method. The reason for this is the anticipated order or magnitude of the polarizabilities of the lithium dimer. We give hereinafter the formulae for the computation of the axial components of the hyperpolarizabilities.

$E_{z,zzz}$ is computed from (4), the octopole moment induced by the quasi homogeneous field of a very distant electric charge:

$$\begin{aligned} E_{z,zzz} &= \frac{R^2}{Q} (\Omega_{zzz}^0 - \Omega_{zzz}(Q, R, 0)) \\ &= -\frac{R^2}{Q} \Omega_{zzz}(Q, R, 0), \end{aligned} \quad (6)$$

where $\Omega_{\alpha\beta\gamma}(Q, R, 0)$ is the octopole moment in the presence of the static field of a charge Q placed at a distance R from the origin, with θ the angle defined by the position vector of the charge and the positive z axis.

$C_{zz,zz}$ and $B_{zz,zz}$ are computed from the induced quadrupole moment as

$$C_{zz,zz} = \frac{R^3}{6Q} (3\Theta_{zz}^0 + \Theta_{zz}(2Q, R, 0) - 4\Theta_{zz}(Q, R, 0)), \quad (7)$$

$$B_{zz,zz} = \frac{R^4}{Q^2} (\Theta_{zz}^0 + \Theta_{zz}(2Q, R, 0) - 2\Theta_{zz}(Q, R, 0)), \quad (8)$$

where $\Theta_{\alpha\beta}(Q, R, 0)$ is defined as in the case of the octopole.

Last γ_{zzzz} is computed from the induced dipole moment as

$$\begin{aligned} \gamma_{zzzz} &= \frac{R^6}{Q^3} (-\mu_z(3Q, R, 0) + 3\mu_z(2Q, R, 0) \\ &\quad - 3\mu_z(Q, R, 0)). \end{aligned} \quad (9)$$

We report also values for the isotropic and anisotropic components of the polarizabilities defined as

$$\bar{\alpha} = \frac{1}{3}(\alpha_{zz} + 2\alpha_{xx}), \quad (10)$$

$$\Delta\alpha = \alpha_{zz} - \alpha_{xx}, \quad (11)$$

$$\bar{C} = \frac{1}{10}(C_{zz,zz} + 8C_{xz,xz} + 8C_{xx,xx}), \quad (12)$$

$$\Delta_1 C = 5C_{zz,zz} + 4C_{xz,xz} - 8C_{xx,xx}, \quad (13)$$

$$\Delta_2 C = 2C_{zz,zz} - 4C_{xz,xz} + C_{xx,xx}, \quad (14)$$

$$\bar{B} = \frac{2}{15}(B_{zz,zz} + 4B_{xz,xz} + B_{xx,zz} + 4B_{xx,xx}), \quad (15)$$

$$\Delta_1 B = B_{zz,zz} + 2B_{xz,xz} - 3B_{xx,zz} - 4B_{xx,xx}, \quad (16)$$

$$\Delta_2 B = 3B_{zz,zz} - 8B_{xz,xz} + 26B_{xx,zz} + 16B_{xx,xx}, \quad (17)$$

$$\Delta_3 B = 3B_{zz,zz} - 8B_{xz,xz} - 2B_{xx,zz} + 2B_{xx,xx}, \quad (18)$$

$$\bar{\gamma} = \frac{1}{15}(3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz}), \quad (19)$$

$$\Delta_1 \gamma = 3\gamma_{zzzz} - 4\gamma_{xxxx} + 3\gamma_{xxzz}, \quad (20)$$

$$\Delta_2 \gamma = \gamma_{zzzz} + \gamma_{xxxx} - 6\gamma_{xxzz}. \quad (21)$$

Atomic units are used throughout this paper. One a.u. of energy is equivalent to 4.3598×10^{-18} J, of length to $0.52917706 \times 10^{-10}$ m, of μ to 8.4784×10^{-30} C m, of Θ to 4.4866×10^{-40} C m², of Ω to 2.3742×10^{-50} C m³, of Φ to 1.2564×10^{-60} C m⁴, of α to 0.16488×10^{-40} C² m² J⁻¹, of γ to 0.62360×10^{-64} C⁴ m⁴ J⁻³, of C or E to 4.6171×10^{-62} C² m⁴ J⁻¹, and of B to 1.6967×10^{-63} C³ m⁴ J⁻².

II. Results and Discussion

We carried out our calculations with a (14s 5p 1d) GTO basis set contracted to [8s 5p 1d]. This set was built upon a (13s 4p)[7s 4p] sp substrate [18] and further enlarged to (14s 5p)[8s 5p] by adding one diffuse s-GTO and one diffuse p-GTO with exponents $0.00985 a_0^{-2}$ and $0.0514 a_0^{-2}$ respectively. The exponents were chosen as to roughly continue the geometric progression of the preceding ones. The final basis set included one d-GTO with exponent $0.01 a_0^{-2}$.

All calculations were performed with this final basis set at the experimental bond length of $5.05 a_0$. The energy and the electric moments were determined by one calculation on the free molecule. Our value for E^0 is $-14.87136799 E_h$ which is only $0.000195 E_h$ higher than the accurate numerical Hartree-Fock result [19]. The agreement is also good

for the respective quadrupole moment which differs only about -0.5% from the numerical result while the hexadecapole moment is somewhat larger (Table 1). Such divergences are to be expected for higher order multipole moments, even close to the Hartree-Fock limit [2 g].

The electric polarizabilities were calculated from the electric dipole, quadrupole and octopole moments induced by the field of charges $+1$, $+2$, and $+3$ placed at a distance $R = 40 a_0$ from the center of mass of the molecule and $\theta = 0$, $\frac{\pi}{4}$ and $\frac{\pi}{2}$. The calculated values are given in Table 1, along with other theoretical results. The two early Time-Dependent Hartree-Fock (TDHF) results predict values for the parallel and perpendicular components for α which are both larger than ours [20, 21]. Our value for α_{zz} is $251 e^2 a_0^2 E_h^{-1}$, in good agree-

Table 1. Electric moments and polarizabilities for $\text{Li}_2(X^1\Sigma_g^+)^a$.

Property	SCF ^b	TDHF ^c	TDHF ^d	SCF ^e	N-HF ^f
Θ_{zz}	10.5783			10.8 ^g	10.632695
Φ_{zzzz}	90.9296				84.09240
α_{zz}	251	256.33	270.39	249.1	
α_{xx}	158	189.09	187.19	179.0	
$\bar{\alpha}$	189	211.50	214.92	202.4	
$\Delta\alpha$	93	83.20	67.24	70.1	
γ_{zzzz}	1900.5×10^3				
γ_{xxxx}	205.2×10^3				
γ_{xxzz}	26.2×10^3				
$\bar{\gamma}$	510.5×10^3				
$\Delta_1 \gamma$	4959.3×10^3				
$\Delta_2 \gamma$	1948.5×10^3				
$C_{zz,zz}$	1377			1625	
$C_{xz,xz}$	994				
$C_{xx,xx}$	693			419	
\bar{C}	1487				
$\Delta_1 C$	5317				
$\Delta_2 C$	-529				
$E_{z,zzz}$	2102			1375	
$E_{x,xxx}$	-320			-750	
$B_{zz,zz}$	-1114×10^2			-115625	
$B_{xz,xz}$	-390×10^2				
$B_{xx,zz}$	159×10^2				
$B_{xx,xx}$	-290×10^2			-28125	
\bar{B}	-490×10^2				
$\Delta_1 B$	-1211×10^2				
$\Delta_2 B$	-728×10^2				
$\Delta_3 B$	-1120×10^2				

^a The center of mass is at the origin (0, 0, 0) with z as the molecular axis. — ^b Present investigation.

^c Time dependent Hartree-Fock [20]. — ^d [21]. — ^e [22b].

^f Numerical Hartree-Fock [19]. — ^g [22a].

ment with the $249.1 e^2 a_0^2 E_h^{-1}$ of Bishop et al. [22b]. However, the good agreement does not extend to the perpendicular components. The basis set used in their study is somewhat smaller than ours, (10s 5p) [5s 5p]. Our calculation of the second dipole hyperpolarizability of Li_2 is, to our knowledge, the first to appear in the literature. The axial component of this property is quite large, $1900.5 \times 10^3 e^4 a_0^4 E_h^{-3}$. As a useful check we computed this property from the perturbed energies too, using a formula similar to (9). We found a value about -0.25% different from the aforementioned one, a proof of the reliability of our approach. Bishop et al. [22b] calculated also the axial and perpendicular components of the C , E and B tensors. For C and E our values are rather different than theirs. The agreement is surprisingly good for $B_{zz,zz}$ and $B_{xx,xx}$ where our values differ from theirs less than 4% in either case, which is more than can be expected for tensors of such high rank.

In Tables 2 and 3 we present the contribution of the multipole moments and static polarizabilities to the interaction of Li_2 with an electron at various distances from the center of mass of the diatomic. The electrostatic and inductive parts of E_{int} are

computed from (1). The expansion in (1) becomes less accurate as the electron approaches close to the molecule i.e. converges slowly and additional terms are required if a more rigorous treatment is to be obtained. It is apparent from Tables 1 and 2 that the hyperpolarizabilities contribute more than substantially to the interaction energy for the relatively shorter distances R . Their importance in intermolecular interaction studies were anticipated in an early paper by Buckingham [17b]. A similar conclusion was reached by Tatewaki and Nakamura [23] who found that in the physisorption of Ar on the ionic crystals Li^+F^- , Na^+Cl^- and K^+Cl^- the contribution of the quadrupole-quadrupole polarizability is as important as that of the dipole one. The higher polarizabilities should also be expected to be of importance in the interpretation of related phenomena, as the interaction of molecules with metal surfaces [24]. The contribution of the B tensor is positive for both the collinear and the perpendicular approaches. As the isotropic component of this tensor was found to be negative for all atomic and molecular systems, at least in the case of the diatomics for the latter, we may conclude that B represents the electrophobic part for the e^- -atom or

Table 2. Contribution of the electric moments and polarizabilities to the $\text{Li}_2\text{-}e^-$ interaction energy, collinear approach ^a.

R	Θ_{zz}	Φ_{zzzz}	α_{zz}	$C_{zz,zz}$	$E_{z,zzz}$	$B_{zz,zz}$	γ_{zzzz}	E_{el}^b	E_{ind}^c	E_{int}^d
7	-0.0308	-0.0054	-0.0523	-0.0176	-0.0179	0.0676	-0.0137	-0.0362	-0.0339	-0.0701
10	-0.0106	-0.0009	-0.0125	-0.0021	-0.0021	0.0056	-0.0008	-0.0115	-0.0119	-0.0234
13	-0.0048	-0.0002	-0.0044	-0.0004	-0.0004	0.0009	-0.0001	-0.0050	-0.0044	-0.0094
16	-0.0027	-0.0001	-0.0019	-0.0001	-0.0001	0.0002	-0.0000	-0.0027	-0.0019	-0.0046
20	-0.0013	-0.0000	-0.0008	-0.0000	-0.0000	0.0000	-0.0000	-0.0013	-0.0008	-0.0021
30	-0.0004	-0.0000	-0.0002	-0.0000	-0.0000	0.0000	-0.0000	-0.0004	-0.0002	-0.0006

^a The center of mass of Li_2 is at the origin (0, 0, 0) with z as the molecular axis and the electron at (0, 0, R) along the positive z axis. — ^b The sum of the contributions of the electric moments.

^c The sum of the contributions of the polarizabilities. — ^d $E_{\text{int}} = E_{\text{el}} + E_{\text{ind}}$.

Table 3. Contribution of the electric moments and polarizabilities to the $\text{Li}_2\text{-}e^-$ interaction energy, perpendicular approach ^a.

R	Θ_{zz}	Φ_{zzzz}	α_{xx}	$C_{xx,xx}$	$E_{x,xxx}$	$B_{xx,xx}$	γ_{xxxx}	E_{el}^b	E_{ind}^c	E_{int}^d
6	0.0245	-0.0044	-0.0610	-0.0223	0.0069	0.0518	-0.0050	0.0201	-0.0296	-0.0095
10	0.0053	-0.0003	-0.0079	-0.0010	0.0003	0.0014	-0.0001	0.0050	-0.0073	-0.0023
15	0.0016	-0.0000	-0.0016	-0.0001	0.0000	0.0001	-0.0000	0.0016	-0.0016	-0.0000
20	0.0007	-0.0000	-0.0005	-0.0000	0.0000	0.0000	-0.0000	0.0007	-0.0005	0.0002
30	0.0002	-0.0000	-0.0001	-0.0000	0.0000	0.0000	-0.0000	0.0002	-0.0001	0.0001

^a The center of mass of Li_2 is at the origin (0, 0, 0) with z as the molecular axis and the electron at (0, R , 0) along the positive x axis. — ^b The sum of the contributions of the electric moments.

^c The sum of the contributions of the polarizabilities. — ^d $E_{\text{int}} = E_{\text{el}} + E_{\text{ind}}$.

e^- -molecule interactions (see [2c] and [4–13] for other \bar{B} values.).

We do not discuss here the effect of electron correlation on the calculated properties as it is beyond the scope of the present work and will be treated in a future paper. For a discussion on the calculation of the dipole polarizability using correlated wavefunctions we refer to Bishop et al. [22b].

III. Conclusions

We have calculated electric polarizabilities and hyperpolarizabilities for the ground state of the

lithium dimer. The reported values should be close to the Hartree-Fock limit. The large internuclear separation of Li_2 accounts for the particularly soft electronic distribution along the molecular axis and leads to very enhanced electric polarizabilities and hyperpolarizabilities.

Acknowledgements

We are grateful to Drs. G. H. F. Diercksen and W. Kraemer for permission to use their programme MUNICH.

- [1] A. D. Buckingham, *Adv. Chem. Phys.* **12**, 107 (1967).
M. P. Bogaard and B. J. Orr, *Int. Rev. Sci. Phys. Chem. Series 2*, Vol. 2 (A. D. Buckingham, ed.) 149 (1975). – A. D. Buckingham, in: *Intermolecular interactions: From diatomics to biopolymers*. John Wiley, New York 1978, pp. 1–67.
- [2] H. J. Werner and W. Meyer, *Mol. Phys.* **31**, 855 (1976). – R. J. Bartlett and G. D. Purvis, *Phys. Rev. A* **20**, 1313 (1979). – D. M. Bishop and L. M. Cheung, *Phys. Rev. A* **20**, 1310 (1979). – P. Lazzeretti and R. Zanassi, *J. Chem. Phys.* **74**, 5216 (1981). – P. W. Fowler and A. D. Buckingham, *Mol. Phys.* **50**, 1349 (1983). – J. Applequist, *Chem. Phys.* **85**, 279 (1984). – D. G. Bounds and S. Wilson, *Mol. Phys.* **54**, 445 (1985). – G. H. F. Diercksen and A. J. Sadlej, *Chem. Phys. Lett.* **114**, 187 (1985). – C. E. Dykstra, *J. Chem. Phys.* **82**, 4120 (1985).
- [3] G. R. Meredith, B. Buchalter, and C. Hanzlik, *J. Chem. Phys.* **78**, 1543 (1983). – T. Lundeen, S. Y. Hou, and J. W. Niebler, *J. Chem. Phys.* **79**, 6301 (1983). – J. W. Dudley II and J. F. Ward, *J. Chem. Phys.* **82**, 4673 (1985).
- [4] G. Maroulis and D. M. Bishop, *Chem. Phys. Lett.* **114**, 182 (1985).
- [5] D. M. Bishop and G. Maroulis, *J. Chem. Phys.* **82**, 2381 (1985).
- [6] G. Maroulis and D. M. Bishop, *Chem. Phys.* **96**, 409 (1985).
- [7] G. Maroulis and D. M. Bishop, *J. Phys. B* **18**, 3653 (1985).
- [8] G. Maroulis and D. M. Bishop, *J. Phys. B*, in press.
- [9] G. Maroulis and D. M. Bishop, *Mol. Phys.*, to be published.
- [10] G. Maroulis and D. M. Bishop, *J. Phys. B*, to be published.
- [11] G. Maroulis and D. M. Bishop, *Theor. Chim. Acta*, to be published.
- [12] G. Maroulis and D. M. Bishop, submitted for publication.
- [13] G. Maroulis and D. M. Bishop, submitted for publication.
- [14] H. F. Schaefer, *J. Chem. Phys.* **62**, 4815 (1975).
- [15] K. Hermann and P. S. Bagus, *Phys. Rev. B* **17**, 4082 (1978). – J. Kendrick and I. H. Hillier, *Mol. Phys.* **33**, 635 (1977). – L. Skala, *Phys. Stat. Sol. b* **107**, 351 (1981). – A. K. Ray, J. L. Fry, and C. W. Myles, *J. Phys. B* **18**, 381 (1985).
- [16] D. M. Bishop and C. Pouchan, *J. Chem. Phys.* **80**, 789 (1984). – D. M. Bishop, M. Chaillet, K. Larrieu, and C. Pouchan, *Mol. Phys.* **51**, 179 (1984).
- [17] A. D. Buckingham and J. A. Pople, *Proc. Phys. Soc. London* **68**, 905 (1955). – A. D. Buckingham, *Quart. Rev.* **13**, 183 (1959).
- [18] F. B. van Duijneveldt, IBM Res. Rep. 945, Dec. 1971. G. C. Lie and E. Clementi, *J. Chem. Phys.* **60**, 1275 (1974).
- [19] D. Sundholm, P. Pykkö, and L. Laaksonen, submitted for publication.
- [20] I. R. Epstein, *J. Chem. Phys.* **53**, 1881 (1970).
- [21] D. K. Watson, R. F. Stewart, and A. Dalgarno, *J. Chem. Phys.* **64**, 4995 (1976).
- [22] D. M. Bishop and C. Pouchan, *Chem. Phys. Lett.* **102**, 132 (1983). – D. M. Bishop, M. Chaillet, C. Larrieu, and C. Pouchan, *Phys. Rev. A* **31**, 2785 (1985).
- [23] H. Tatewaki and T. Nakamura, *Surf. Sci.* **108**, L 447 (1981).
- [24] H. S. Luftman and J. M. White, *Surf. Sci.* **139**, 369 (1984).