

Calculation of dynamic polarizabilities
and long-range dispersion energy coefficients:
application to the alkali metal atoms

by

J.J.C.Teixeira-Dias and L.M.C.Simões

Chemical Laboratory of the
University of Coimbra, Portugal

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Abstract

The results previously obtained for the dynamic polarizabilities of the hydrogen atom and the long-range dispersion energy coefficients between hydrogen atoms by the Karplus and Kolker variation-perturbation method (J.J.C.Teixeira-Dias and A.J.C. Varandas, 1973, Molec. Phys., 25, 1185) are compared with the results obtained by the differentiation of the Chen and Dalgarno functionals (Molec. Physics, 1965, 9, 349) for the same systems. After showing the value of using frequency-dependent Slater-type functions optimized by the differentiation of the Karplus and Kolker functionals (J. chem. Phys., 1968, 39, 1493) the authors show that this approach is also reliable for many-electron systems providing the number of frequency-dependent functions can be reduced to one or two as the optimization of non-linear variables (the orbital exponents) becomes a time-consuming procedure when the number of optimizable orbitals increases. As an example, the dynamic polarizabilities of the alkali-metal atoms and the long-range dispersion energy coefficients for pairs of these atoms are calculated.

1. INTRODUCTION

In the theory of long-range intermolecular forces the dispersion energy is usually expanded in inverse powers of R , $E_D = -(C_6 R^{-6} + C_8 R^{-8} + \dots)$, where the coefficients describe the interactions between the various induced multipole moments of different molecules. For spherically symmetric systems in their ground states and after averaging the interaction energy over all their relative orientations we have

$$C_K^{AB} = \frac{(2m+2n)!}{2\pi(2m)!(2n)!} \int_0^\infty \alpha_A^{(m)}(i\omega) \alpha_B^{(n)}(i\omega) d\omega \quad (1)$$

and

$$\alpha_A^{(m)}(u) = \frac{8\pi}{2m+1} \sum_{s=1}^{\infty} \frac{\Delta E_{s0}^A |\langle \psi_0^A | \hat{r}_i^m Y_m^0(\hat{r}_i) | \psi_s^A \rangle|^2}{\Delta E_{s0}^A{}^2 - (\hbar u)^2} \quad (2)$$

where $k = 2(m+n+1)$, $\Delta E_{s0}^A = E_s^A - E_0^A$, $Y_m^0(\hat{r}_i)$ is the usual spherical harmonic, $u = i\omega$ and $\alpha_A^{(m)}(i\omega)$ represents the 2^m -pole dynamic polarizability of system A at the frequency ω . The evaluation of the dynamic polarizabilities is not a straightforward calculation as (2) requires a summation over an infinite number of states and includes an integral over the continuum.

As it happens in the frequency-independent case, (2) has a very slow convergence especially when the unperturbed excited states are used and a substantial contribution to it comes from the matrix elements involving the continuum [1-3]. Moreover, although for many systems approximate ground-state functions are available, almost nothing is known about the excited state functions.

In the evaluation of $\alpha^{(m)}(i\omega)$ we have used a previously formulated variational method [2] to obtain approximate solutions for the time-dependent first-order perturbation equations which result from the interaction between a system (atom or molecule) and a periodic electric field oscillating at the angular frequency ω . The infinite summation (2) is then replaced by a similar expression consisting of a finite sum over frequency-dependent functions. The object of this paper is to see how a simple basis set of pseudostates, when used in variational calculations, greatly reduces the labour in the

evaluation of the dynamic polarizabilities and leads to a quick convergence of the variational solution.

Using the values of $\alpha_H^{(1)}(i\omega)$ and $\alpha_H^{(2)}(i\omega)$ thus obtained we have calculated the dispersion energy coefficients C_6^{HH} , C_8^{HH} and the quadrupole-quadrupole contribution to the R^{-10} interaction in reasonable agreement with the exact values.

2. THE VARIATION-PERTURBATION METHOD

The first-order perturbation equation which results from the solution of the time-dependent Schrödinger equation for a system of hamiltonian $H^0(\underline{r})$ in the presence of a time-dependent perturbation $H'(\underline{r}, t)$, is

$$H^0(\underline{r}) \psi^{(1)}(\underline{r}, t) + H'(\underline{r}, t) \psi^{(0)}(\underline{r}, t) = i \dot{\psi}^{(1)}(\underline{r}, t) \quad (3)$$

where $\psi^{(0)}(\underline{r}, t)$ is the unperturbed eigenfunction and $\psi^{(1)}(\underline{r}, t)$ is the first-order wavefunction (we use atomic units and so $\hbar = 1$). The dynamic electric polarizabilities of a system can be calculated by considering its interaction with a linearly polarized electric field. If this is periodic and ^{of} angular frequency ω we can separate the time-dependence in $H'(\underline{r}, t)$ by the relationship

$$H'(\underline{r}, t) = G^{(m)}(\underline{r}) \{ \exp(i\omega t) + \exp(-i\omega t) \} \quad (4)$$

where $G^{(m)}(\underline{r})$ is the 2^m pole operator.

The steady-state solution of (3) can be written as

$$\psi^{(1)}(\underline{r}, t) = \psi_-(\underline{r}) \exp[-i(\omega_n + \omega)t] + \psi_+(\underline{r}) \exp[-i(\omega_n - \omega)t] \quad (5)$$

where $\omega = \frac{E}{\hbar}$ ($\hbar = 1$) and $\psi_+(\underline{r})$ and $\psi_-(\underline{r})$ satisfy the time-independent first-order perturbation equations

$$\{ H^0(\underline{r}) - E^0 + \omega \} \psi_+(\underline{r}) = -G^{(m)}(\underline{r}) \psi^0(\underline{r}) \quad (6)$$

and $\psi^0(\underline{r}, t) = \psi^0(\underline{r}) \exp(-i\omega_n t)$. If we now consider arbitrary $\tilde{\psi}_+(\underline{r})$ and $\tilde{\psi}_-(\underline{r})$ as Karplus and Kolker [2], and define, $\tilde{L}_+^{(m)}$ and $\tilde{L}_-^{(m)}$ by

$$\tilde{L}_{\pm}^{(m)} = -\langle \psi_{\pm}(\underline{r}) | H^0(\underline{r}) - E_{\pm}^0 + \omega | \psi_{\pm}(\underline{r}) \rangle + 2 \langle \psi_{\pm}(\underline{r}) | G^{(m)}(\underline{r}) | \psi_0(\underline{r}) \rangle \quad (7)$$

then it is well known that

$$(\delta \tilde{L}_{\pm}^{(m)})_{\omega} = 0 \quad (8)$$

are the variational principles for solution of the equations (6). If the functions used to construct the first-order time-independent wavefunction,

$$\tilde{\psi}_{\pm}(\underline{r}) = \sum_{i=1}^n c_i^{\pm} \theta_i \quad (9)$$

satisfy the conditions [4]

$$\left. \begin{aligned} i) \quad \langle \theta_i | \theta_j \rangle &= \delta_{ij} \\ ii) \quad \langle \theta_i | \psi_0 \rangle &= 0 \\ iii) \quad \langle \theta_i | H^0 | \theta_j \rangle &= E_i^0 \delta_{ij} \end{aligned} \right\} \quad (10)$$

and the functionals $\tilde{L}_{\pm}^{(m)}$ are differentiated with respect to the c_i^{\pm} 's, we obtain

$$\tilde{L}_{\pm}^{(m)} = - \sum_{i=1}^n \frac{\langle \theta_i | G^{(m)}(\underline{r}) | \psi_0 \rangle^2}{\Delta E_{i0} \pm \hbar \omega} \quad (11)$$

and

$$\alpha^{(m)}(\omega) = -(\tilde{L}_{+}^{(m)} + \tilde{L}_{-}^{(m)}) \quad (12)$$

3. RESULTS AND DISCUSSION

a) *The hydrogen atom : previous values [5] compared with new results*

If the summation in (9) is restricted, for the calculation of the dipole dynamic polarizability, to one Slater-type $2p$ orbital of variable ζ exponent the conditions (10) are automatically fulfilled and the functionals $\tilde{L}_+^{(1)}$ and $\tilde{L}_-^{(1)}$ depend parametrically on the $2p$ orbital exponent. Their differentiation with respect to ζ at constant ω ,

$$\left(\frac{\partial \tilde{L}_\pm}{\partial \zeta}\right)_\omega = 0 \quad (13)$$

yields a relationship between ω and ζ which defines the optimum $2p$ orbital exponent, ζ_{opt} , for each separate frequency (cf. Teixeira-Dias et al, [5]):

$$\omega = \pm(7\zeta_{opt}^3 - 9\zeta_{opt}^2 + 9\zeta_{opt} - 5)/[10(1-\zeta_{opt})] \quad (14)$$

Table 1 shows the optimized exponents thus obtained and the corresponding $\alpha_H^{(1)}(i\omega)$ values [5].

The simplicity of the wavefunction as compared with the four-term wavefunction used by Chan and Dalgarno [6] to construct the basis for their variation calculation and the excellent agreement obtained emphasize the importance of optimizing the frequency-dependent exponent for the $2p$ orbital.

In order to assess the effect of using gaussian functions in the calculation we have also included a single gaussian orbital of the $2p$ type in the variational calculation for the hydrogen atom dipole polarizability. The differentiation of the functionals $\tilde{L}_\pm^{(1)}$ with respect to the exponent at each separate frequency yields the results in table 2. Although these values are low compared with the exact results of Chan and Dalgarno, the dispersion energy coefficient thus obtained ($C_6^{HH} = \frac{5.846}{\cancel{6.788}}$) compares well with the result obtained by Singh and Meath [7] ($C_6^{HH} = 5.7679$) using a gaussian orbital with a frequency-independent exponent in a two-centre dispersion energy calculation. The value of using an optimized frequency-dependent orbital is thus also shown when the

Gaussian functions are used as basis functions in the variational calculation in spite of the fact that these basis functions did not manage to reproduce the exact values so well as Slater-type functions. Therefore, we decide to restrict ourselves to the Slater-type functions as basis functions for the construction of the solutions of our variational calculation and refer now to a different variational procedure used by Chan and Dalgarno [6].

This variational method is based on the minimization of the functional

$$\tilde{J}^{(m)}(\omega) = \langle \tilde{\phi}(\underline{r}) | (\hat{H}^0 - E^0)^2 + \omega^2 | \tilde{\phi}(\underline{r}) \rangle + 2 \langle \tilde{\phi}(\underline{r}) | G^{(m)}(\underline{r}) | \psi^0(\underline{r}) \rangle \quad (15)$$

with respect to the trial function $\tilde{\phi}(\underline{r})$. If this functional is used to optimize the exponent of a single $2p$ orbital, the values thus obtained (table 1) are lower at small frequencies than the results obtained by the differentiation of the $\tilde{L}_+^{(m)}$ and $\tilde{L}_-^{(m)}$ functionals.

When the $2p$ eigenfunction of the hydrogen atom hamiltonian is included in the basis set and the resulting set of $2p$ orbitals transformed in order to fulfil the conditions (10), the results show some improvement especially near the first transition frequency and $C_6^{HH} = 6.202$ as compared with $C_6^{HH} = 6.511$ [5],

So far we have exemplified, in the case of the hydrogen atom, the importance of using frequency-dependent functions optimized by the differentiation of the Karplus and Kolker functionals $\tilde{L}_\pm^{(m)}$ at each separate frequency for the calculation of the dynamic dipole polarizability. The method has also been successfully applied to the calculation of the hydrogen atom quadrupole polarizabilities [5] and yielded good values for the dynamic polarizabilities of the helium atom and for the long-range dispersion energy coefficients between helium atoms [8]. The main object of this work is to show that this approach is also reliable for many-electron systems providing the number of frequency-dependent functions can be reduced to one or two as the optimization of non-linear variables (the orbital exponents) becomes a time-consuming procedure when the number of optimizable orbitals increases.

b) *The lithium and sodium atoms*

We have, therefore, chosen to calculate the dynamic polarizabilities of the alkali metal atoms and the long-range dispersion energy coefficients for pairs of these atoms.

The model used for the alkali metal is considered to consist of a "~~frozen~~^{frozen} inert-atom core" plus the valence electron whose wavefunction is represented analytically by the SCF Clementi function [12]. The excited pseudostate used in the basis for the variational calculation is a single Slater-type orbital with a frequency-dependent exponent. It is further assumed that the functional dependence between the energy of the excited pseudostate and the frequency-dependent exponent is given by the expectation value of the hydrogen ^{atom} hamiltonian for that orbital as the effective charge experienced by the excited electron should be close to one. Hence the optimized exponent obtained by the differentiation of (11) accounts also for the departure between the hydrogen atom potential ~~of the core~~^{of the core} assumed for the excited electron and the self-consistent field potential as well as for the neglect of the requirements of the antisymmetry in the wavefunction. The excited pseudostates thus optimized for the lithium and sodium atoms and the dipole and quadrupole polarizabilities at imaginary frequencies are shown in tables 3 and 4. The long-range dispersion energy coefficients C_6 , C_8 and C_{10} (quadrupole-quadrupole) have been calculated for $\omega < 100$ using the trapezoidal rule. The dipole and quadrupole polarizabilities at $\omega=0$ and the long-range dispersion energy coefficients are compared in tables 5 and 6 with previously reported values. Both the static polarizabilities and the C_6 coefficients are in reasonable agreement with previous values calculated using more elaborate models. A question that now arises consists in deciding how to choose the frequency-dependent excited pseudostates to include in the basis for the variational calculation. We do not have a definite criterium although a possible solution for this question may consist in choosing those pseudostates that yield, after optimization, the best values for the static polarizabilities. As the energy differences between the frequency-

-dependent pseudostates previously considered ($3p_z$ and $3d_z^2$ for the lithium atom; $4p_z$ and $4d_z^2$ for the sodium atom) and the ground-state as represented analytically by the Clementi function for the valence electron are almost constant over the whole range of frequencies (for example, $E_{Li}(3p_z)$ varies between -0.1188 A.U. at $\omega=0$ and -0.1183 A.U. at $\omega=100$ and $E_{Li}(3d_z^2)$ varies in the range -0.0471 A.U. at $\omega=0$ and -0.0393 A.U. at $\omega=100$), the above procedure is equivalent to the scaling of the calculated value of C_6^{AB} by the factor

$$\frac{(\alpha_A^{(1)})_{exp} (\alpha_B^{(1)})_{exp}}{(\alpha_A^{(1)})_{calc} (\alpha_B^{(1)})_{calc}} \quad (16)$$

where the polarizabilities refer to $\omega=0$. We have not used any scaling factors for the lithium and sodium atoms as the functions included in the basis for the variational calculations yielded good values for the static polarizabilities of these atoms. However, for the potassium atom, the first trial frequency-dependent functions we have used so far ($5p_z$ and $5d_z^2$) give high values for the static polarizabilities and for the C_6 coefficient ($\alpha_K^{(1)}=420.2$ A.U. and $\alpha_K^{(2)}=6650$ A.U., $C_6^{KK}=6530$). If, in this case, we use for $(\alpha_K^{(1)})_{exp}$ the values derived by Dalgarno and Kingston [10] and include them in (16) the resulting $C_6^{KK}=2915$ acquires the right magnitude and becomes close to the results reported by these authors ($C_6^{KK}=3820$). These values are still high compared with the experimental results. Possible reasons for this fact are reviewed in [15].

As to the C_8 and C_{10} (*quad-quad*) results we obtained it is important to briefly refer a few points. First of all no experimental values are found in the literature. In fact, in analyzing the experimental data it is necessary to introduce a model potential function containing certain parameters which are then adjusted so as to reproduce the observations as closely as possible. Now the potential function normally used consists of one attractive term ($-C_6/R^6$) and one expression consisting of one or more repulsive

terms, no allowance being usually made for the $-C_8/R^8$ and $-C_{10}/R^{10}$ terms. Secondly, the theoretical values often quoted are the results obtained by Fontana[16] which were evaluated using a screened hydrogenic system with an effective nuclear charge determined from optical spectra. These results are too low to reasonably agree with experiment. Though we admit that the values we obtained for C_8 and C_{10} (*quad-quad*) are, on the contrary, somewhat high, we believe that they are sufficiently valid to mean that the R^{-8} and higher terms in the dispersion energy expansion are far from negligible and that, in these circumstances, the use of perturbation theory may be inappropriate.

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Karplus and Kolker functionals, (7)Chan and Dalgarno functional, (15)

ω	$\zeta_{opt} [5]$	$\alpha^{(1)}(i\omega) [5]$	ζ_{opt} (this work)	$\alpha^{(1)}(i\omega)$
0.0	0.7970	4.475 (0)	0.6844	4.267 (0)
0.2	0.8364	3.666 (0)	0.7050	3.457 (0)
0.4	0.8618	2.421 (0)	0.7478	2.250 (0)
0.6	0.8800	1.565 (0)	0.7906	1.458 (0)
0.8	0.8936	1.055 (0)	0.8265	9.942 (-1)
1.0	0.9044	7.464 (-1)	0.8554	7.131 (-1)
1.2	0.9131	5.516 (-1)	0.8785	5.336 (-1)
1.4	0.9203	4.225 (-1)	0.8971	4.129 (-1)
1.6	0.9264	3.331 (-1)	0.9121	3.284 (-1)
1.8	0.9315	2.690 (-1)	0.9242	2.670 (-1)
2.0	0.9360	2.215 (-1)	0.9343	2.211 (-1)
4.0	0.9612	5.919 (-2)	0.9781	6.022 (-2)
6.0	0.9721	2.682 (-2)	0.9896	2.730 (-2)
8.0	0.9782	1.523 (-2)	0.9940	1.547 (-2)
10.0	0.9821	9.797 (-3)	0.9961	9.936 (-3)
50.0	0.9961	3.984 (-4)	0.9998	3.999 (-4)
100.0	0.9980	9.960 (-5)	1.0000	9.999 (-5)
		$C_6^{HH} = 6.548$		$C_6^{HH} = 5.849$

Table 1. The dipole polarizability of atomic hydrogen at imaginary frequencies and the long-range dispersion energy coefficients. The single 2p Slater-type function used in the basis set was optimized for each separate frequency. Both the frequency and the polarizabilities are in atomic units. The numbers in parenthesis under α are powers of 10 by which α is to be multiplied.

ω	ζ_{opt}	$\alpha_H^{(1)}(i\omega)$
0.0	0.1250	4.158 (0)
0.2	0.1250	4.158 (0)
0.4	0.1417	2.316 (0)
0.6	0.1463	1.510 (0)
0.8	0.1498	1.021 (0)
1.0	0.1525	7.230 (-1)
1.2	0.1547	5.340 (-1)
1.4	0.1565	4.085 (-1)
1.6	0.1581	3.217 (-1)
1.8	0.1594	2.594 (-1)
2.0	0.1605	2.134 (-1)
4.0	0.1667	5.654 (-2)
6.0	0.1694	2.551 (-2)
8.0	0.1708	1.445 (-2)
10.0	0.1718	9.280 (-3)
50.0	0.1751	3.752 (-4)
100.0	0.1755	9.392 (-5)

$C_6^{HH} = 5.846$

Table 2. The dipole polarizability of atomic hydrogen at imaginary frequencies and the long-range dispersion energy coefficient C_6 . The basis set included a single excited pseudo-state represented by a gaussian function of the $2p$ type with an optimized frequency-dependent exponent. All the values are in atomic units.

ω	$\zeta_{opt}(3p_z)$	$\alpha_{Li}^{(1)}(i\omega)$	$\zeta_{opt}(3d_z^2)$	$\alpha_{Li}^{(2)}(i\omega)$
0.0	0.6822	1.485 (2)	0.4634	1.453 (3)
0.2	0.6673	1.949 (1)	0.4868	5.307 (2)
0.4	0.6635	5.412 (0)	0.4953	1.850 (2)
0.6	0.6619	2.456 (0)	0.4997	8.901 (1)
0.8	0.6609	1.392 (0)	0.5024	5.164 (1)
1.0	0.6603	8.943 (-1)	0.5042	3.356 (1)
2.0	0.6590	2.247 (-1)	0.5085	8.586 (0)
4.0	0.6582	5.625 (-2)	0.5111	2.163 (0)
6.0	0.6580	2.501 (-2)	0.5120	9.631 (-1)
8.0	0.6579	1.407 (-2)	0.5124	5.422 (-1)
10.0	0.6578	9.00 (-3)	0.5127	3.472 (-1)
100.0	0.6575	9.0 (-5)	0.5138	3.48 (-3)

Table 3. The dipole and quadrupole polarizabilities of atomic lithium at imaginary frequencies. The $3p_z$ and $3d_z^2$ Slater-type functions used in the basis set were optimized for each separate frequency. All the values are in atomic units. The numbers in parenthesis under α are powers of 10 by which α is to be multiplied,

ω	$\zeta_{opt}(4p_z)$	$\alpha_{Na}^{(1)}(i\omega)$	$\zeta_{opt}(4d_z^2)$	$\alpha_{Na}^{(2)}(i\omega)$
0.0	0.8279	1.876 (2)	0.5809	2.211 (3)
0.2	0.8087	2.220 (1)	0.6049	6.915 (2)
0.4	0.8044	6.101 (0)	0.6126	2.276 (2)
0.6	0.8025	2.763 (0)	0.6165	1.077 (2)
0.8	0.8015	1.565 (0)	0.6188	6.204 (1)
1.0	0.8008	1.005 (0)	0.6204	4.017 (1)
2.0	0.7993	2.523 (-1)	0.6239	1.021 (1)
4.0	0.7985	6.316 (-2)	0.6259	2.567 (0)
6.0	0.7982	2.808 (-2)	0.6266	1.142 (0)
8.0	0.7981	1.580 (-2)	0.6270	6.428 (-1)
10.0	0.7980	1.011 (-2)	0.6272	4.115 (-1)
100.0	0.7977	1.0 (-4)	0.6281	4.12 (-3)

Table 4. The dipole and quadrupole polarizabilities of atomic sodium at imaginary frequencies. The $4p_z$ and $4d_z^2$ Slater-type functions used in the basis set were optimized for each separate frequency. All the values are in atomic units. The numbers in parenthesis under α are powers of 10 by which α is to be multiplied.

<i>atom</i>	$\alpha^{(1)}(\omega=0)$	$\alpha^{(2)}(\omega=0)$	<i>reference</i>
<i>Li</i>	148.5	1452.8	<i>this work</i>
	146.4	1494.2	[9], (<i>coupled H-F</i>)
	164.7±16.5		[10]
	135.0±20		[11], (<i>experimental</i>)
<i>Na</i>	187.6	2211.0	<i>this work</i>
	166.0±17		[10]
	135 ±17		[11], (<i>experimental</i>)

Table 5. The dipole and quadrupole atomic polarizabilities of lithium and sodium atoms at $\omega=0$ compared with previously reported values. All the results are in atomic units.

<i>interaction</i>	C_6	C_8	C_{10} (quad.-quad.)	<i>reference</i>
<i>Li ... Li</i>	1286	8.3×10^4	2.8×10^6	<i>this work</i>
	1380	-	-	[13]
<i>Na ... Na</i>	1932	14.8×10^4	5.8×10^6	<i>this work</i>
	1580	-	-	[13]
	920	-	-	[14]

Table 6. The long-range dispersion energy coefficients for pairs of lithium and sodium atoms. All values are in atomic units.

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