On the application of the variation–perturbation method of Karplus and Kolker to the calculation of the Van der Waals energies between alkali atoms†

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In two previous papers [1, 2] the dynamic polarizabilities of the hydrogen and helium atoms and the long-range dispersion energy coefficients between pairs of these atoms have been calculated by the variation–perturbation method proposed by Karplus and Kolker [3]. The calculations were performed within a one-centre model approach. It was shown that simple first-order wave-functions built up from one or two Slater-type functions with frequency-dependent exponents optimized by the differentiation of the Karplus and Kolker functionals [3] and subject to the conditions used in [1], yielded good values for the dynamic polarizabilities and the long-range dispersion energy coefficients. In our opinion, this approach provides a simple and quick method of estimating long-range interatomic parameters with reasonable accuracy. In this work we apply the same method to the calculation of the dynamic polariza-bilities and long-range dispersion energy coefficients of the alkali-metal atoms.

It is well known that the differentiation of the functionals

$$\tilde{L}_{\pm}^{(m)} = -\langle \tilde{\phi}_{\pm}^{(1)}(\mathbf{r})/H^{(0)} - E^{(0)} \pm \hbar i\omega/\tilde{\phi}_{\pm}^{(1)}(\mathbf{r})\rangle$$
$$+ 2\langle \tilde{\phi}_{\pm}^{(1)}(\mathbf{r})/G^{(m)}(\mathbf{r})/\phi^{(0)}(\mathbf{r})\rangle \quad (1)$$

with respect to the variational parameters included in the expression of $\tilde{\phi}_{\pm}^{(1)}(\mathbf{r})$, $(\delta \tilde{L}_{\pm}) = 0$, provides approximations to the first-order time-independent functions $\phi_{\pm}^{(1)}(\mathbf{r})$ [3] ($G^{(m)}(\mathbf{r})$ is the 2^m-pole operator and $i\omega$ represents the imaginary frequency). In particular, if

$$\tilde{\phi}_{\pm}^{(1)}(\mathbf{r}) = \sum_{i=1}^{n} c_i^{\pm} \theta_i, \quad (2)$$

where the functions θ_i diagonalize the unperturbed hamiltonian, $H^{(0)}$, and are orthogonal to the ground-state eigenfunction $\phi^{(0)}(\mathbf{r})$, the stationary values of $\tilde{L}_{\pm}$ with respect to variations in the the coefficients $c_i^{\pm}$ yield

$$\tilde{L}_{\pm}^{(m)} = -\sum_{i=1}^{n} \frac{\langle \theta_i/G^{(m)}(r)/\phi^{(0)}\rangle^2}{\Delta \tilde{E}_{i0} \pm i\hbar\omega}. \quad (3)$$

The atomic model used to calculate (3) consists of a non-polarizable inert-atom core plus the valence electron whose ground-state wavefunction is represented analytically by the SCF Clementi function [4]. The excited pseudostate used in the basis for the variational calculation is a single Slater-type orbital with

the frequency-dependent exponent, ζ. It is also assumed that the functional dependence between the energy of the excited pseudostate and ζ is given by the hydrogenic value for that orbital as the effective charge experienced by the 'excited electron' should be close to one [5]. Hence, the optimized exponent obtained from $(\partial \tilde{L}_{\pm}/\partial \zeta)_{\omega} = 0$ accounts also for the departure between the hydrogenic potential and the self-consistent potential of the core as well as for the neglect of the requirements of the antisymmetry in the wavefunction.

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. One could consider the effective principal quantum number, n^*, of the frequency-dependent Slater-type orbital, as a variational parameter, and optimize $\tilde{L}_{\pm}$ with respect to both ζ and n^*. However, the inclusion of n^* as an additional non-linear parameter to optimize requires numerical integrations in the evaluation of (3) and increases very much the computing time. In view of the simplicity of the wavefunctions we use and of the discrepancies among the previously reported values of the static polarizabilities and dispersion energy coefficients, we think that an optimization of $\tilde{L}_{\pm}(\zeta, n^*)$ with respect to n^* would only increase the labour of the calculation.

We have chosen the Slater-type functions to include in the basis for the variational calculation of $\alpha^{(m)}(i\omega)$ from an inspection of the values they give to the excitation energies, oscillator strengths and static polarizabilities. Before we pass on and look at these values, it is perhaps important to mention that the values of the static dipole and quadrupole polarizabilities of the alkali-metal atoms are dominated by the contributions of the first resonance transitions [6–8]. If a two-term representation of the dipole polarizability at imaginary frequencies, $\alpha(i\omega) = \tilde{f}_1/(\Delta \tilde{E}_{10}^2 + \hbar^2\omega^2) + \tilde{f}_2/(\Delta \tilde{E}_{20}^2 + \hbar^2\omega^2)$, is used to reproduce optical data of the alkali-metal atoms and the value of $\tilde{f}_1$ is fixed at the oscillator strength value of the first resonance transition, then the first term gives a contribution which exceeds, at zero frequency, 98 per cent in all cases [6]. In table 1 we present the

Atom	Pseudostates and references	$\Delta \tilde{E}_{10}$	$\tilde{f}_1$	$\tilde{\alpha}^{(1)} = \tilde{f}_1/\Delta \tilde{E}_{10}^2$
Li	$2p_z(0\cdot4848)$	$0\cdot0714$	$0\cdot805$	$158\cdot0$
	$3p_z(0\cdot6822)$	$0\cdot0775$	$0\cdot892$	$148\cdot5$
	[6]	$0\cdot068$	$0\cdot75$	162
Na	$3p_z(0\cdot6627)$	$0\cdot0637$	$0\cdot869$	$214\cdot2$
	$4p_z(0\cdot8279)$	$0\cdot0730$	$1\cdot000$	$187\cdot6$
	$5p_z(0\cdot9848)$	$0\cdot0821$	$1\cdot112$	$165\cdot0$
	[6]	$0\cdot077$	$0\cdot98$	165
K	$4p_z(0\cdot7618)$	$0\cdot0399$	$0\cdot802$	$503\cdot6$
	$5p_z(0\cdot8852)$	$0\cdot0487$	$0\cdot997$	$420\cdot2$
	$6p_z(1\cdot0085)$	$0\cdot0564$	$1\cdot154$	$362\cdot8$
	$7p_z(1\cdot1323)$	$0\cdot0631$	$1\cdot275$	$320\cdot1$
	$8p_z(1\cdot2587)$	$0\cdot0693$	$1\cdot176$	$244\cdot9$
	[6]	$0\cdot059$	$1\cdot01$	290

Table 1. The excitation energy $(\Delta \tilde{E}_{10})$ and the oscillator strength $(\tilde{f}_1)$ of the pseudo dipole transition at zero frequency, and the static dipole polarizability compared with the values of ω_1, f_1 and f_1/ω_1^2 taken from table 3 of [6]. The numbers in parentheses are the exponents optimized at zero frequency.

values of the excitation energies, oscillator strengths and static dipole polarizabilities calculated using different Slater-type functions to represent the excited pseudostates orbitals, and the corresponding values of those quantities taken from the first term in the analytical representation of $\alpha^{(1)}(i\omega)$ [6]. From this table we have selected the orbitals which are then used to represent the single excited pseudostates in the calculation of the optimized exponents at each separate frequency and of the dipole polarizabilities at imaginary frequencies (table 2).

As to the quadrupole polarizabilities, the results we present in table 3 show that the choice of the Slater-type function used to represent the excited pseudostate in the quadrupole transition is not so critical as it was for the evaluation of the dipole properties. Moreover, there are few accurate values of the quadrupole polarizabilities reported in the literature which can be used for comparison.

$\hbar\omega$	$\zeta_{opt}(2p_z)$	$\alpha_{Li}^{(1)}(i\omega)$		$\zeta_{opt}(5p_z)$	$\alpha_{Na}^{(1)}(i\omega)$		$\zeta_{opt}(7p_z)$	$\alpha_K^{(1)}(i\omega)$	
0·0	0·4848	1·580	(2)	0·9848	1·650	(2)	1·1323	3·201	(2)
0·2	0·4752	1·794	(1)	0·9798	2·382	(1)	1·1169	2·909	(1)
0·4	0·4727	4·908	(0)	0·9787	6·679	(0)	1·1141	7·808	(0)
0·6	0·4715	2·221	(0)	0·9781	3·037	(0)	1·1130	3·519	(0)
0·8	0·4708	1·257	(0)	0·9778	1·722	(0)	1·1123	1·989	(0)
1·0	0·4704	8·072	(−1)	0·9776	1·106	(0)	1·1119	1·276	(0)
2·0	0·4694	2·027	(−1)	0·9772	2·780	(−1)	1·1111	3·200	(−1)
4·0	0·4689	5·073	(−2)	0·9770	6·958	(−2)	1·1106	8·006	(−2)
6·0	0·4687	2·255	(−2)	0·9769	3·093	(−2)	1·1105	3·559	(−2)
8·0	0·4686	1·269	(−2)	0·9769	1·740	(−2)	1·1104	2·002	(−2)
10·0	0·4686	8·12	(−3)	0·9769	1·114	(−2)	1·1103	1·281	(−2)
100·0	0·4684	8·0	(−5)	0·9768	1·1	(−4)	1·1102	1·3	(−4)

Table 2. The dipole polarizabilities of atomic lithium, sodium and potassium at imaginary frequencies. The Slater-type functions used in the basis for the variational calculation were optimized at each separate frequency. All the values are in atomic units. The numbers in parentheses under α are powers of 10 by which α is to be multiplied. a.u. dipole polarizability $= 4\pi\epsilon_0 a_0^3 \simeq 0·164878 \times 10^{-40}$ C² m² J⁻¹.

Atom	Pseudostates and references	$\Delta\tilde{E}_{20}$	$\tilde{f}_2$	$\tilde{\alpha}^{(2)} = \tilde{f}_2/\Delta\tilde{E}_{20}^2$
Li	$3d_{z^2}(0·4634)$	0·1492	32·4	1453
	$4d_{z^2}(0·6062)$	0·1497	32·8	1466
	[8]	—	36·9 ± 0·6	1413 ± 26
Na	$4d_{z^2}(0·5809)$	0·1333	39·3	2211
	$5d_{z^2}(0·7140)$	0·1356	39·9	2167
K	$5d_{z^2}(0·6297)$	0·0964	61·8	6650
	$6d_{z^2}(0·7437)$	0·0989	63·0	6442
	$7d_{z^2}(0·8560)$	0·1016	64·0	6193

Table 3. The excitation energy ($\Delta\tilde{E}_{20}$) and the oscillator strength $\tilde{f}_2$) of the pseudo quadrupole transition at zero frequency, and the static quadrupole polarizability. The numbers in parenthesis are the exponents optimized at zero frequency.

$\hbar\omega$	$\zeta_{opt}(3d_{z^2})$	$\alpha_{Li}^{(2)}(i\omega)$		$\zeta_{opt}(5d_{z^2})$	$\alpha_{Na}^{(2)}(i\omega)$		$\zeta_{opt}(7d_{z^2})$	$\alpha_K^{(2)}(i\omega)$	
0·0	0·4634	1·453	(3)	0·7140	2·167	(3)	0·8560	6·193	(3)
0·2	0·4868	5·307	(2)	0·7416	6·934	(2)	0·8814	1·286	(3)
0·4	0·4953	1·850	(2)	0·7504	2·298	(2)	0·8878	3·822	(2)
0·6	0·4997	8·901	(1)	0·7548	1·089	(2)	0·8907	1·762	(2)
0·8	0·5024	5·164	(1)	0·7574	6·275	(1)	0·8924	1·004	(2)
1·0	0·5042	3·356	(1)	0·7592	4·064	(1)	0·8935	6·469	(1)
2·0	0·5085	8·586	(0)	0·7632	1·033	(1)	0·8959	1·632	(1)
4·0	0·5111	2·163	(0)	0·7655	2·597	(0)	0·8972	4·090	(0)
6·0	0·5120	9·631	(−1)	0·7663	1·156	(0)	0·8976	1·819	(0)
8·0	0·5124	5·422	(−1)	0·7667	6·504	(−1)	0·8979	1·023	(0)
10·0	0·5127	3·472	(−1)	0·7669	4·164	(−1)	0·8980	6·550	(−1)
100·0	0·5138	3·48	(−3)	0·7679	4·17	(−3)	0·8985	6·55	(−3)

Table 4. The quadrupole polarizabilities of atomic lithium, sodium and potassium at imaginary frequencies. The Slater-type functions used in the basis for the variational calculation were optimized at each separate frequency. All the values are in atomic units. The numbers in parentheses under α are powers of 10 by which α is to be multiplied.
a.u. quadrupole polarizability $= 4\pi\epsilon_0 a_0^5 \simeq 0.461705 \times 10^{-61}$ C^2 m^4 J^{-1}.

Table 4 shows the optimized exponents and the quadrupole polarizabilities at imaginary frequencies calculated with the functions we have chosen.

The integrals which relate the long-range dispersion energy coefficients with the polarizabilities at imaginary frequencies have been calculated for $\hbar\omega \leqslant 100$ a.u.† using the trapezoidal rule. Both the static polarizabilities and the long-range dispersion energy coefficients agree reasonably well with previously reported values (tables 5 and 6). In particular, the values we obtained for C_8 and C_{10} (quad–quad) agree well with the results obtained by Kultzelnigg using a two-centre approach where the influence of the core electrons was represented by a 'cut-off' pseudopotential [9].

Atom	$\alpha^{(1)}(\omega=0)$	$\alpha^{(2)}(\omega=0)$	References
Li	158·0	1453	This work
	167·9 ± 0·3	1413 ± 26	[7, 8]
	135·0 ± 20		[10], exp.
	162·9		[6]
Na	165·0	2167	This work
	135 ± 17		[10], exp.
	166·1		[6]
K	320·1	6193	This work
	243 ± 30		[10], exp.
	290·9		[6]

Table 5. The static dipole and quadrupole atomic polarizabilities compared with previously reported values. All the results are in atomic units.

† a.u. frequency = hartree/$\hbar \simeq 4.134138 \times 10^{16}$ Hz.

Interaction	C_6	C_8	C_{10}(quad–quad)	References
Li...Li	1340	$8\cdot4 \times 10^4$	$2\cdot8 \times 10^6$	This work
	1458 ± 8	84070 ± 2883		[7, 8]
	1230	$8\cdot4 \times 10^4$	$2\cdot8 \times 10^6$	[9]
	1380 (9)	—	—	[6]
Na...Na	1679	$1\cdot4 \times 10^5$	$5\cdot6 \times 10^6$	This work
	1588	$1\cdot2 \times 10^5$	$4\cdot3 \times 10^6$	[9]
	1580 (40)	—	—	[6]
	920	—	—	[11], exp.
K...K	4859	$5\cdot8 \times 10^5$	$3\cdot4 \times 10^7$	This work
	4040	$4\cdot0 \times 10^5$	$2\cdot04 \times 10^7$	[9]
	3680 (420)	—	—	[6]
	1590	—	—	[11], exp.

Table 6. The long-range dispersion energy coefficients for pairs of lithium, sodium and potassium atoms. The values given in parentheses are estimates of the core contributions. All values are in atomic units.

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