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REGULAR ARTICLE

Rank-1 approximation to the van der Waals interaction

Yet another formula for dispersion constants

Gian Luigi Bendazzoli

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Abstract We present and discuss a variational single-product approximation to the van der Waals dispersion interaction leading to a simple formula for C_6 that seems capable to give more than 99% of the 'exact' value. The formula is derived from Hylleraas' variational principle in the tensor product space of the interacting molecules and therefore enjoys bounding properties. The formula has been tested by computing the C_6 dispersion constants of H–H, and, at Full CI level, of the following systems: He–He, He–Li, Li–Li, LiH–LiH, HF–HF. Connections with the London formula are discussed.

1 Introduction

The interaction of two molecules A, B at large distance R can be treated as a perturbation theory (PT) problem in the tensor product space of the interacting molecules (A–B exchange neglected) [1,2]. In particular, the first order PT equation for the dispersion interaction can be written as follows [3]:

$$\left[(\hat{H}^A - E_0^A) + (\hat{H}^B - E_0^B)\right]\Phi^d = -(Q_1^A - \hat{Q}^A)\Phi_0^A \times (Q_1^B - \hat{Q}^B)\Phi_0^B \tag{1}$$

where

$$\begin{aligned} &\hat{H}^A|\Phi_0^A\rangle = E_0^A|\Phi_0^A\rangle; \quad \hat{H}_B|\Phi_0^B\rangle = E_0^B|\Phi_0^B\rangle \\ &Q_1^A = \langle\Phi_0^A\hat{Q}^A|\Phi_0^A\rangle_A; \quad Q_1^B = \langle\Phi_0^B\hat{Q}^B|\Phi_0^B\rangle_B \end{aligned} \tag{2}$$

where $\hat{Q}^A$, $\hat{Q}^B$ are multipole operators centered on A, B, and $\langle\ |\ \rangle_A$, $\langle\ |\ \rangle_B$ mean scalar product in the space of molecule A and B, respectively. (for C_6, $\hat{Q} = a^\mu$, dipole lenght operator). In order to simplify the notation we introduce the shorthands:

$$\theta^A = |(Q_1^A - \hat{Q}^A)\Phi_0^A\rangle, \quad \theta^B = |(Q_1^B - \hat{Q}^B)\Phi_0^B\rangle \tag{3}$$

so the r.h.s. of Eq. (1) can be written as $-\theta^A\theta^B$. The dispersion energy can be computed as a sum of contributions of the type:

$$\langle\Phi^d|\theta^A\theta^B\rangle_{AB} \tag{4}$$

where $\langle|\rangle_{AB}$ is the scalar product in the (tensor) product space of the interacting molecules. The exact solution of Eq. (1) can be represented in several ways [3], the most important in this context being the Casimir–Polder integral representation [4]:

$$\Phi^d = -\frac{2}{\pi}\int_0^{+\infty}\left(\frac{\hat{H}^A - E_0^A}{(\hat{H}^A - E_0^A)^2 + \omega^2}\theta^A\right) \times \left(\frac{\hat{H}^B - E_0^B}{(\hat{H}^B - E_0^B)^2 + \omega^2}\theta^B\right)\mathrm{d}\omega \tag{5}$$

i.e. by a linear superposition of products of functions of molecule A and functions of molecule B labelled by the continuous variable ω. In a series of papers [5–8], Kutzelnigg and collaborators introduced the natural state expansion:

$$\Phi^d = \sum_i d_i\, u_i^A v_i^B,\ i = 1, 2, \ldots \tag{6}$$

u_i^A, v_i^B are normalized eigenfunctions of suitably defined molecular density matrices in the supermolecular system $A \cdots B$. Expansion (6) enjoys remarkable

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G. L. Bendazzoli (✉)
Dipartimento di Chimica Fisica ed Inorganica,
Università di Bologna, Bologna, Italy
e-mail: oskar@ms.fci.unibo.it

convergence properties and a single term was found to give surprisingly good accuracy for atoms [6].

In this paper we consider a single product or rank-1 approximation for Φ^d:

$$\Phi^d \approx -\tilde{\Phi}^A \tilde{\Phi}^B = \tilde{\Phi} \tag{7}$$

where $\tilde{\Phi}$ and its factors $\tilde{\Phi}^A$ and $\tilde{\Phi}^B$ are variationally determined, and we obtain from the ansatz (7) a formula for matrix elements (4). Equation (7) can be considered as the expansion (6) truncated to one term and written in a slightly different way. According to Hylleraas' variational principle [9] we determine $\tilde{\Phi}^A$ and $\tilde{\Phi}^B$ minimizing the functional (real perturbations):

$$\begin{aligned} Hy[\tilde{\Phi}^A, \tilde{\Phi}^B] = \Big\langle \tilde{\Phi}^A \tilde{\Phi}^B | \hat{H}^A - E_0^A + \hat{H}^B \\ - E_0^B | \tilde{\Phi}^A \tilde{\Phi}^B \Big\rangle_{AB} \\ + 2\langle \tilde{\Phi}^A \tilde{\Phi}^B | \theta^A \, \theta^B \rangle_{AB} \end{aligned} \tag{8}$$

subject to the constraints:

$$\langle \tilde{\Phi}^A | \Phi_0^A \rangle_A = \langle \tilde{\Phi}^B | \Phi_0^B \rangle_B = 0 \tag{9}$$

The plan of the paper is the following: we work out the equations determining the best $\tilde{\Phi}^A$, $\tilde{\Phi}^B$ and the new formula, we specialize the formalism to the Full CI case (FCI) and, finally, we compute the C_6 of some systems at FCI level. A discussion is given in the last section.

2 The equations for the optimal rank-1 $\tilde{\Phi}$

We introduce two Lagrange multipliers λ^A and λ^B to account for the constraints (9), and write down the minimum conditions:

$$\begin{aligned} \frac{1}{2}\frac{\delta Hy}{\delta \tilde{\Phi}^A} = \langle \tilde{\Phi}^B | \tilde{\Phi}^B \rangle_B (\hat{H}^A - E_0^A) \tilde{\Phi}^A \\ + \langle \tilde{\Phi}^B | (\hat{H}^B - E_0^B) \tilde{\Phi}^B \rangle_B \tilde{\Phi}^A \\ - \langle \tilde{\Phi}^B | \theta^B \rangle_B \theta^A - \lambda^A \Phi_0^A = 0 \end{aligned} \tag{10}$$

$$\begin{aligned} \frac{1}{2}\frac{\delta Hy}{\delta \tilde{\Phi}^B} = \langle \tilde{\Phi}^A | \tilde{\Phi}^A \rangle_A (\hat{H}^B - E_0^B) \tilde{\Phi}^B \\ + \langle \tilde{\Phi}^A | (\hat{H}^A - E_0^A) \tilde{\Phi}^A \rangle_A \tilde{\Phi}^B \\ - \langle \tilde{\Phi}^A | \theta^A \rangle_A \theta^B - \lambda^B \Phi_0^B = 0 \end{aligned} \tag{11}$$

By left multiplying Eqs. (10,11) by Φ_0^A and Φ_0^B, respectively, and integrating we find $\lambda^A = \lambda^B = 0$. Next, we introduce the quantities:

$$\omega_A = \frac{\langle \tilde{\Phi}^A | (\hat{H}^A - E_0^A) \tilde{\Phi}^A \rangle_A}{\langle \tilde{\Phi}^A | \tilde{\Phi}^A \rangle_A}, \quad \omega_B = \frac{\langle \tilde{\Phi}^B | (\hat{H}^B - E_0^B) \tilde{\Phi}^B \rangle_B}{\langle \tilde{\Phi}^B | \tilde{\Phi}^B \rangle_B} \tag{12}$$

that can be described as averaged excitation energies associated to the trial functions $\tilde{\Phi}^A$, $\tilde{\Phi}^B$, and notice that, thanks to Eq. (9), they are greater or equal to the first excitation energy of the molecule:

$$\omega_A \ \geq \ E_1^A - E_0^A \ > \ 0, \quad \omega_B \ \geq \ E_1^B - E_0^B \ > \ 0 \tag{13}$$

The extremal conditions (11,10) can be rewritten as

$$(\hat{H}^A - E_0^A + \omega_B) \tilde{\Phi}^A \ = \ c_B \theta^A \tag{14}$$

$$(\hat{H}^B - E_0^B + \omega_A) \tilde{\Phi}^B \ = \ c_A \theta^B \tag{15}$$

where c_A, c_B stand for:

$$c_A = \frac{\langle \tilde{\Phi}^B | \theta^B \rangle_B}{\langle \tilde{\Phi}^B | \tilde{\Phi}^B \rangle_B}, \quad c_B = \frac{\langle \tilde{\Phi}^A | \theta^A \rangle_A}{\langle \tilde{\Phi}^A | \tilde{\Phi}^A \rangle_A} \tag{16}$$

Therefore, $\tilde{\Phi}^A$ is given by the solution ξ_A of the equation

$$(\hat{H}^A - E_0^A + \omega_B) \xi_A = \theta^A \tag{17}$$

multiplied by c_B, i.e. $\tilde{\Phi}^A = c_B \xi_A$, and similarly $\tilde{\Phi}^B$. By left multiplying Eq. (14) by $\tilde{\Phi}^A$, integrating and dividing by $\langle \tilde{\Phi}^A | \tilde{\Phi}^A \rangle_A$, we find $\omega_A + \omega_B = c_A \, c_B$.

The variational solution $\tilde{\Phi} = -\tilde{\Phi}^A \tilde{\Phi}^B$ of our problem has the form

$$\begin{aligned} \tilde{\Phi} \ = \ -(\omega_A + \omega_B) \ (\hat{H}^A - E_0^A + \omega_B)^{-1} \theta^A \\ \times (\hat{H}^B - E_0^B + \omega_A)^{-1} \theta^B \end{aligned} \tag{18}$$

and $Hy[\tilde{\Phi}^A, \tilde{\Phi}^B]$ becomes a function of the variables ω_A and ω_B that can be assumed as variational parameters. As concerns the quantities c_A and c_B, only their product is uniquely defined; this holds as well for the functions $\tilde{\Phi}^A$ and $\tilde{\Phi}^B$.

To carry out the minimisation of (8) it is convenient to introduce the quantities

$$\begin{aligned} G_k^\sigma(\omega) \ = \ \langle \theta^\sigma | (\hat{H}^\sigma - E_0^\sigma + \omega)^{-k} | \theta^\sigma \rangle_\sigma, \\ \sigma = A, \, B, \quad k = 1, \, 2, \, \ldots \end{aligned} \tag{19}$$

After little algebra we find that Eq. (8) can be written as a sum of two terms:

$$Hy(\omega_A, \, \omega_B) = F(\omega_A, \omega_B) + V(\omega_A, \omega_B) \tag{20}$$

where

$$F(\omega_A, \omega_B) = -(\omega_A + \omega_B) \ \ G_1^A(\omega_B) G_1^B(\omega_A) \tag{21}$$

and

$$\begin{aligned} V(\omega_A, \omega_B) = - \ (\omega_A + \omega_B) \\ \times \Big[G_1^A(\omega_B) - (\omega_A + \omega_B) G_2^A(\omega_B) \Big] \\ \times \Big[G_1^B(\omega_A) - (\omega_A + \omega_B) G_2^B(\omega_A) \Big] \end{aligned} \tag{22}$$

As concerns the derivatives of the Hylleraas' functional, we easily find

$$\frac{\partial Hy}{\partial \omega_A} = -\left[G_1^A(\omega_B) - (\omega_A+\omega_B)G_2^A(\omega_B)\right] \times \left\{3(\omega_A+\omega_B)^2 G_3^B(\omega_A) - 4(\omega_A+\omega_B)G_2^B(\omega_A) + 2G_1^B(\omega_A)\right\}, \text{etc.} \tag{23}$$

As shown in Appendix 1, the quantity in curly braces in the previous equation (23) cannot vanish, so the optimal $\omega_A,\ \omega_B$ are solutions of the following non linear coupled equations:

$$G_1^A(\omega_B) - (\omega_A+\omega_B)G_2^A(\omega_B) = 0 \tag{24}$$

$$G_1^B(\omega_A) - (\omega_A+\omega_B)G_2^B(\omega_A) = 0 \tag{25}$$

We observe that $V(\omega_A,\omega_B)$ defined by Eq. (22) vanishes at the solution of Eqs. (24 and 25); consequently, the optimum value of $Hy(\omega_A,\omega_B)$ is given by $F(\omega_A,\omega_B)$ alone when $\omega_A,\ \omega_B$ fulfill Eqs. (24 and 25). Equation (21) defines the functional $F(\omega_A,\omega_B)$ and it is our new formula for the dispersion interaction; its practical application requires the solution of the coupled equations (24, 25).

As a first test of Eq. (21) we consider the long range dispersion interaction of two hydrogen atoms in their ground state. In this case $\hat{Q}$ is the dipole operator $\hat{\mu}$, $\hat{H}^A = \hat{H}^B$, $\theta^A = \theta^B$, $\omega_A = \omega_B = \omega$, and the formulae (20, 21) reduce to

$$F(\omega) = -2\omega[G_1(\omega)]^2 \tag{26}$$

$$Hy(\omega) = F(\omega) - 2\omega[G_1(\omega) - 2\omega G_2(\omega)]^2 \tag{27}$$

We remind that for two atoms in S states [2] $C_6 = 6\,\langle ZZ|ZZ\rangle_{AB}$, where we used the following notation for matrix elements (4) involving the cartesian components of the dipole operator:

$$\langle XY|XY\rangle_{AB} = \left\langle \theta_X^A\theta_Y^B \right| \left(\hat{H}^A - E_0^A + \hat{H}^B - E_0^B\right)^{-1} \left. \theta_X^A\theta_Y^B \right\rangle_{AB} \tag{28}$$

$$\theta_X^A = \left(\hat{\mu}_X^A - \langle \Phi_0^A|\hat{\mu}_X^A|\Phi_0^A\rangle_A\right)\Phi_0^A, \ \text{etc} \tag{29}$$

Explicit formulae of the matrix elements G_k for hydrogen atom are given in [10] in terms of hypergeometric functions and the quantity (26) can easily be computed. In Fig. 1 we report: (i) the new functional (curve F) Eq. (26), (ii) Hylleraas' functional (curve Hy) Eq. (27) and (iii) the exact value (line Ex). By numerical solution of the Eq. (24) for $\omega_A = \omega_B = \omega$ we find the optimal value $\bar{\omega}$, and from it we compute $C_6 = -6F(\bar{\omega})$. The results are $\bar{\omega} = 0.439529$ and $C_6 = 6.49711$, i.e. the value reported by Maeder and Kutzelnigg [6]. Using $C_6 = 6.49903$ as the exact value for $H \cdots H$ dispersion constant truncated to five decimals, we have an error of 0.02%. The exact C_6 has been independently obtained by many authors, see, e.g. [11–16] with a high number of decimals.

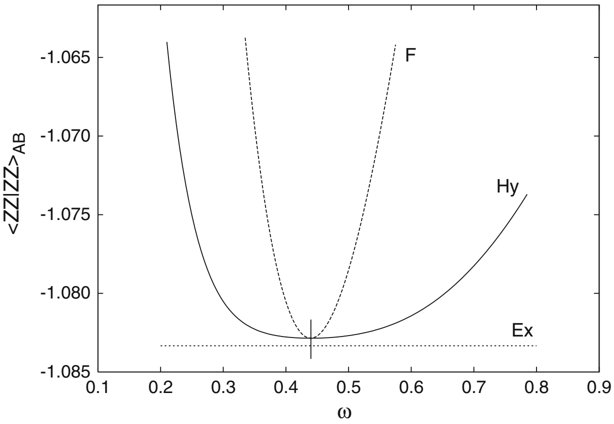

Fig. 1 Different approximations to the $\langle ZZ|ZZ\rangle_{AB}$ matrix element for interacting hydrogen atoms as functions of ω: curve F, new formula Eq. (26), curve Hy, Hylleraas' functional Eq. (27). The line labelled (Ex) marks the exact value. All quantities are in atomic units

The new functional Eq. (26) appears to be more sensitive than Hylleraas' to displacements of ω from the minimum $\bar{\omega}$. As expected, $\bar{\omega}$ is greater than the first excitation energy of hydrogen (0.375 h).

3 The dispersion interaction between two systems at Full CI level

In the FCI case, the functions Φ_0^σ, θ^σ, $\tilde{\Phi}^\sigma$, and $\sigma = A, B$ are expanded, for each molecule, in a basis of orthonormal Slater's determinants ς_k^σ, $k = 1, 2, \ldots N_\sigma$ as follows:

$$\begin{aligned} \Phi_0^\sigma &= \sum_{k=1}^{N_\sigma} \varsigma_k^\sigma c_k^\sigma = (\boldsymbol{\varsigma}^\sigma)^T \mathbf{c}^\sigma, \\ \theta^\sigma &= \sum_{k=1}^{N_\sigma} \varsigma_k^\sigma b_k^\sigma = (\boldsymbol{\varsigma}^\sigma)^T \mathbf{b}^\sigma \end{aligned} \tag{30}$$

The perturbative Eq. (1) is replaced by

$$\left[(\mathbf{H}^A - E_0^A) \otimes \mathbf{I}^B + \mathbf{I}^A \otimes (\mathbf{H}^B - E_0^B)\right] \boldsymbol{\Phi}^d = -\mathbf{b}^A \otimes \mathbf{b}^B \tag{31}$$

$$\mathbf{b}^A = (E_1^A - \mathbf{Q}^A)\mathbf{c}^A,\ \mathbf{b}^B = (E_1^B - \mathbf{Q}^B)\mathbf{c}^B \tag{32}$$

where $\mathbf{H}^\sigma$, $\mathbf{Q}^\sigma$ are the matrices of hamiltonian and multipole operators in the FCI space of molecule σ and $\otimes$ is

Kronecker's product. The vector $\boldsymbol{\Phi}^d$ stands to the exact solution of Eq. (1) as the Full CI eigenvector to the exact solution of the molecular Schrödinger's equation, and the matrix elements computed from it according to Eq. (4) are the natural benchmark to test the rank-1 approximation.

We describe first how the benchmarks have been computed in this work and then we present the rank-1 approximation. We used the numerical method proposed in [17] that will be, here, briefly reminded. The solution $\boldsymbol{\Phi}^d$ is expanded as a linear combination of Kronecker products of vectors $\mathbf{z}_p^A$, $\mathbf{z}_q^B$ belonging to the FCI spaces of molecule A and B respectively:

$$\boldsymbol{\Phi}^d = \sum_{pq} c_{pq}\, \mathbf{z}_p^A \otimes \mathbf{z}_q^B \tag{33}$$

The coefficients c_{pq} are determined by variational principles. The number of components of $\boldsymbol{\Phi}^d$ is equal to the product $N_A\, N_B$ of the FCI's dimensions, i.e. it is really huge, but only the vectors $\mathbf{z}_p^A$, $\mathbf{z}_q^B$ need to be handled in the computer code. The expansion vectors are solutions of perturbative equations of the type

$$(\mathbf{H}^A - E_0^A + \omega_i)^k \mathbf{z}^A = \mathbf{b}^A; \quad i, k = 1, 2, \ldots \text{ etc.} \tag{34}$$

at a set of frequencies ω_1, ω_2, … for $k = 1, 2, \ldots$. For $k = 1$, Eq. (34) is required to compute the polarizability of one of the interacting molecules. A satisfactory convergence requires a dozen or so of vectors [17]. Once Eq. (31) is solved, the matrix elements of interest are computed as

$$\sum_{pq} c_{pq} \left[(\mathbf{b}^A)^T \mathbf{z}_p^A\right] \quad \left[(\mathbf{b}^B)^T \mathbf{z}_q^B)\right] \tag{35}$$

which replaces Eq. (4). The quantities computed using the Eqs. (33) and (35) will be, here, referred to as 'full rank'.

Alternatively, we could have used the classical Casimir–Polder numerical integration. As discussed in [17], in a FCI context the method here used presents some advantages, including variational bounds and better convergence. Here we will only remind that Casimir–Polder numerical integration is included in Eq. (35) as a particular choice of expansion vectors and a non variational choice for the coefficients $c_{pq} = \delta_{pq} w_p / 2\pi$, w_p being the weigths of the numerical quadrature. A comparison of the computational cost of the procedures will also be given in Sect. 4.

In this FCI context the rank-1 ansatz Eq. (18) becomes

$$\tilde{\boldsymbol{\Phi}}^d = -(\omega_A + \omega_B)\mathbf{z}^A \otimes \mathbf{z}^B \tag{36}$$

where $\mathbf{z}^A$, $\mathbf{z}^B$ are functions of ω_B, ω_A, defined as solutions of Eq. (34) for $k = 1$ and at the values $\bar{\omega}_A$, $\bar{\omega}_B$, determined by solving Eqs. (24) and (25) by Newton's or similar methods. The matrix elements of Eq. (4) are computed as

$$(\omega_A + \omega_B)\left[(\mathbf{b}^A)^T \mathbf{z}^A(\omega_B)\right] \quad \left[(\mathbf{b}^B)^T \mathbf{z}^B(\omega_A)\right] \tag{37}$$

We remark that this formalism applies to any linear space expansion of the molecular wavefunctions, e.g. truncated CI's.

3.1 The interaction of two atoms at Full CI level

We examined the dipole–dipole dispersion interaction of He and Li. The details of the FCI calculations, performed in D_{2h} symmetry using the method described in [18], are reported in Table 1. ΔE is the excitation energy, α is the dipole polarizability and TRK is the Thomas–Reiche–Kuhn sum rule test [9]. Energies are in hartree, polarizabilities in a_0^3 $(4\pi\epsilon_0 = 1)$, see [2].

Table 2 reports the results for the dispersion constant C_6 for H, He, Li atoms in their ground states. $C_{6\,FRk}$ is the full rank value computed by numerical solution of Eq. (31) using the method of Ref. [17], i.e. Eq. (35); $C_{6\,Rk1}$ is the rank-1 value computed using Eq. (37) at the values $\bar{\omega}_A$, $\bar{\omega}_B$ fulfilling Eqs. (24) and (25). The error of

Table 1 Details of the FCI computations on helium and lithium atoms

He: basis spdfg ACV5Z 80 AO's					
State	N	Energy	ΔE	α	TRK
He 1^1S	964	–2.903201	0.0	1.38299[a]	2.0022136
He 1^1P	840	–2.046357	0.856843	–	–
Li: basis spdfgh CC-PV5Z 105 AO's					
State	N	Energy	ΔE	α	TRK
Li 1^2S	76,604	–7.473439	0.0	164.3666[b]	3.007456
Li 1^2P	73,328	–7.405518	0.067920		–

N is the number of the Slater determinants of the FCI in D_{2h}, ΔE is the excitation energy, α is the dipole polarizability and TRK is the Thomas–Reiche–Kuhn sum rule test [9]. Energies are in hartree, polarizabilities in a.u. a_0^3, see [2]

[a] Compare with $\alpha_{\text{best}} = 1.383192174$ from [19]

[b] Compare with $\alpha_{\text{best}} = 164.111$ from [19]

Table 2 Computed values of C_6 and excitation energies $\bar{\omega}$ for He and Li atoms

	He··· He	Li··· Li	He··· Li
$C_{6\ FRk}$	1.459408	1397.7220	22.53555
$C_{6\ Rk1}$	1.458047	1397.4516	22.52031
Error(%)	0.09	0.02	0.07
$\bar{\omega}_{\mathrm{He}}$	1.068711	–	0.987229
$\bar{\omega}_{\mathrm{Li}}$	–	0.0696635	0.0861086
$C_{6\ \mathrm{best}}$ [19]	1.460978	1393.39	22.507

FRk means full rank or benchmark value, *Rk*1 means rank-1 approximation

Table 3 Computed values of C_6 and excitation energies $\bar{\omega}$ for H–He and H–Li

H ··· X		
	X=He	X=Li
$C_{6\ Rk1}$	2.818852	66.61342
$\bar{\omega}_H$	0.453498	0.423520
$\bar{\omega}_X$	1.02438	0.0759371
$\bar{\omega}_{X-X}$	1.068711	0.06966351
$\bar{\omega}_{H-H}$	0.439529	
$C_{6\ \mathrm{best}}$ [19]	2.821343	66.536

*Rk*1 means rank-1 approximation

Table 4 Details of the FCI calculations of LiH and HF

Molecule	State	N	Energy	ΔE
LiH	$1^1\Sigma^+$	697,753	–8.036925	0.000000
LiH	$2^1\Sigma^+$	697,753	–7.906196	0.130730
LiH	$1^1\Pi$	683,072	–7.869563	0.167363
Electrical properties of LiH $1^1\Sigma^+$				
	μ	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\bar{\alpha}$
This work	2.316	26.666	30.531	29.242
Tunega et al. [22]	2.294	25.79	29.57	28.31
Cafiero et al.[a]	2.2918	25.50	–	–
Molecule	State	N	Energy	ΔE
HF	$1^1\Sigma^+$	19,602,925	–100.180684	–
HF	$2^1\Sigma^+$	19,602,925	–99.641963	0.538721
HF	$1^1\Pi$	19,602,700	–99.798913	0.381771
Electrical properties of HF $1^1\Sigma^+$				
	μ	$\alpha_{\parallel}$	$\alpha_{\perp}$	$\bar{\alpha}$
This work	0.6808	6.142	5.267	5.559
Maroulis [b]	0.7043	6.36	5.22	5.60
Cybulski et al. [c]	–	–	–	5.918
Kumar and Meath DOSD [27]		–	–	5.60

The LiH bond length is assumed 3.015 bohr, the AO basis amounts to 58 CGTO, (10s6p4d/6s4p3d)+1f for Li and (6s4p/4s3p)+2d for H. As concerns HF, the bond length is 1.73289795 bohr, the AO basis is the 24 CGTO Z3 6s3p/3s1p of Sadlej et al. [21], and the $1s^2$ is frozen

[a] $R_e = 3.00$ [23]

[b] $R_e = 1.7328$ [24]

[c] $R_e = 1.7325$ [25]

the rank-1 ansatz, defined with respect to $C_{6\ FRk}$, is very small, less than 0.1%. In the same table the best value $C_{6\ \mathrm{best}}$ available in the literature (to our knowledge) is also reported [19].

In Table 3 we report the results for the dispersion interaction H··· X, where X = He, Li treated at the Full CI level, while for H atom the (exact) closed formulae of [10] were used. In this case we did not compute the quantity corresponding to C_{6FRk}, and therefore the error is omitted. However, we expect a behaviour similar to that reported in the previous Table 2.

As concerns the naure of the stationary point of functional (21) we found minima when $A = B$ and saddle points for $A \neq B$.

3.2 The interaction of two molecules at Full CI level

We report the results of calculations on LiH and HF. The AO bases considered are of lower quality than those used for the atomic calculations, but we think that they illustrate as well the properties of the rank-1

Table 5 Dispersion matrix elements, optimal values $\bar{\omega}$ and isotropic dispersion constant C_6^{000} for LiH . . . LiH and HF . . . HF.

LiH ··· LiH				
	$\langle ZZ\vert ZZ\rangle_{AB}$	$\langle XZ\vert XZ\rangle_{AB}$	$\langle XX\vert XX\rangle_{AB}$	C_6^{000}
FRk	18.09143	20.60035	23.51265	129.696
Rk1	17.98009	20.52519	23.46179	129.285
Error(%)	0.62	0.36	0.22	0.32
$\bar{\omega}_x$	–	0.230753	0.23339	–
$\bar{\omega}_z$	0.214973	0.216282	–	–
HF ··· HF				
	$\langle ZZ\vert ZZ\rangle_{AB}$	$\langle XZ\vert XZ\rangle_{AB}$	$\langle XX\vert XX\rangle_{AB}$	C_6^{000}
FRk	3.893080	3.367922	2.914873	19.350
Rk1	3.887938	3.363141	2.910361	19.321
Error(%)	0.13	0.14	0.15	0.15
$\bar{\omega}_x$	–	0.920939	0.923855	–
$\bar{\omega}_z$	0.884558	0.887147	–	–
Method		Author		C_6^{000}
DOSD		Kumar and Meat [27]		19.00
Pseudo DOSD		Knowles and Meath [26]		16.487
MBPT		Rijks et al. [28]		20.75
Scaled TDHF		Cybulski et al. [25]		19.20

ansatz. In Table 4 we report the details of the FCI calculations; both were performed in C_{2v} symmetry using the method described in [18]. The LiH bond length is assumed to be 3.015 bohr, the AO basis amounts to 58 CGTO, (10s6p4d/6s4p3d)+1f for Li and (6s4p/4s3p)+2d for H and it is the same used in [20]. As concerns HF, the bond length is 1.73289795 bohr, the AO basis is the 24 CGTO Z3 6s3p/3s1p of Sadlej et al. [21], and the $1s^2$ was kept frozen. In this case the AO basis is rather small, although optimized for polarizability calculations.

In Table 5 we display the computed values of matrix elements for the LiH$\cdots$LiH and HF$\cdots$HF dispersion constants. As concerns notation, we use Eq. (28) with Z axis parallel to the bond. The isotropic dispersion constant $C_6^{000} = \frac{2}{3}(\langle ZZ|ZZ\rangle_{AB} + 4\langle XZ|XZ\rangle_{AB} + 4\langle XX|XX\rangle_{AB})$ is also reported.

As concerns the naure of the stationary point of functional (21) we found minima only when $A = B$ and the matrix element is of type $\langle XX|XX\rangle$, i.e. the same dipole component on both molecules; in all other cases, saddle points. The error of the rank-1 approximation is again small ($<1\%$), although larger than for atoms. In case of HF there are a number of values of C_6 available in the literature that can be compared with those computed in this work; they are reported in the lower part of Table 5. The values of C_6^{000} computed show remarkable agreement with the ‘experimental’ DOSD value of Kumar and Meat [27] in spite of the small size of the Z3 basis set.

4 Discussion and conclusions

From the data reported in Tables 2, 3 and 5 the rank-1 ansatz appears to provide an extremely good approximation to the full rank results, confirming the predictions of Kutzelnigg et al. [5–8]. As a further remark to this point, we remind that Eq. (31) can be cast in the form of a matrix Sylvester equation with a rank-1 right hand side [17]. The latter are well known in the field of optimal control theory and mathematical arguments to explain this behaviour can be found, e.g. in [29].

As far as computational cost is concerned, we can compare three different procedures for the computation of dispersion constants in the context of FCI, namely: (A) computing the polarizability at a set of imaginary frequencies and using the values in a Casimir–Polder numerical quadrature; (B) using the ‘full rank’ numerical method of solution here used to provide the benchmark and described in [17]; (C) solving Eqs. (24) and (25) and using the rank-1 formula (37). The comparison between methods A and B has been given in [17], but it will be here reminded for sake of completeness. All alternatives require the same basic ingredients, i.e. the FCI wavefunctions of the monomers and a number of solution vectors of perturbative equations for computing frequency dependent polarizabilities of the monomers. The computational cost is dominated by the application of the hamiltonian $\mathbf{H}$ to a vector $\mathbf{x}$ to produce the vector $\mathbf{y} = \mathbf{Hx}$, also known as the σ-vector [30]. Let’s call C_σ this cost and, for sake of simplicity, consider the computation of a matrix element $\langle XZ|XZ\rangle_{AB}$ contributing to C_6 between two molecules.

(A) In the Casimir–Polder method we solve iteratively n perturbative equations at a prescribed set of imaginary frequencies $\{i\omega_1, i\omega_2, \ldots i\omega_n\}$. Assuming an average number of iterations M per point, we have a computational cost $2nMC_\sigma$ for each monomer, where the factor two is due to the complex frequency. The total cost is therefore $4nMC_\sigma$.

(B) For each imaginary frequency $\{i\omega_1, i\omega_2, \ldots i\omega_n\}$ we get a solution that gives two expansion vectors for Eq. (35), i.e. its real and imaginary parts. For each expansion vector another 'fundamental operation' is required [17], and this brings the cost to $4n(M+1)C_\sigma$. However, as shown in [17] method B converges faster than A, i.e. a smaller number of frequencies is needed to get results of the same quality; roughly speaking, about a half. The cost can be estimated as $(M+1)/2M$ that of method A.

(C) As shown in Fig. 1 for H...H, the functional F depends critically upon the values of ω_A, ω_B and the coupled Eqs. (24) and (25) must be solved by Newton's or similar methods. Each Newton iteration implies the solution of two perturbative equations at real frequency for the monomers, with cost $2MC_\sigma$. The critical factor is the number N of Newton's iterations required, which in turn depends upon the starting values of ω_A, ω_B. Since we do not know any prescription to define good starting values, the total cost $2NMC_\sigma$ is rather unpredictable. In our experience, starting from values close to the first excitation energies, we found on the average costs smaller than but comparable to method B. This feature limits the value of the rank-1 method as a practical computational tool. Moreover, while A and B converge to the same result, method C is only an approximation to it, although very accurate.

Therefore we think that method B should be preferred in a FCI context as a computational tool; the rank-1 approximation owes its interest to the capability to include a surprising accuracy to the common result of A and B in a very simple formula Eq. (21).

Given this performance of Eq. (21), it is tempting to look for some physical significance hidden in it, but we were not able to find one. However we can find a connection with London's formula [2,32,33] for C_6. For this purpose, we remind that the dynamic polarizability is related to Eq. (19) as follows:

$$\alpha(\omega) = G_1(\omega) + G_1(-\omega) \tag{38}$$

as a result of a perturbation theory treatment with a time dependent harmonic field of frequency ω [31]. Since $\omega > 0$, Eqs. (21) and (26) involve only the first term $G_1(\omega)$ of (38), that one called anti-resonant because it is without poles. Following Tang [34], we use Padé [0/1] approximation to $G_1(\omega)$, and write

$$G_1(\omega) \approx \frac{\alpha/2}{1+\omega/U} \tag{39}$$

where α is the static dipole polarizability and U is an effective excitation energy, i.e. we adopt Unsöld's approximation [35]. The functional Eq. (26) becomes

$$F(\omega_A, \omega_B) \approx -\frac{1}{4}(\omega_A+\omega_B)\frac{\alpha_A\alpha_B}{(1+\omega_B/U_A)(1+\omega_A/U_B)} \tag{40}$$

and by minimization we find for the optimal ω's:

$$\omega_A = U_B, \quad \omega_B = U_A, \quad \text{and} \quad F_{\min} = -\frac{1}{4}\,\frac{U_A U_B}{U_A+U_B}\,\alpha_A\alpha_B \tag{41}$$

The C_6 dispersion constant for two atoms in S states becomes

$$C_6 = -6F_{min} = \frac{3}{2}\frac{U_A U_B}{U_A+U_B}\,\alpha_A\alpha_B \tag{42}$$

which is precisely London's formula.

Table 6 Comparison of Unsöld mean energies U computed from C_6 via Eq. (42) and rank-1 $\bar{\omega}$ values from Eqs. (24) and (25)

System	H . . . H	He . . . He	Li . . . Li	He . . . He	Li . . . Li
C_6	6.499027[a]	1.458047 [b]	1397.452[b]	1.460978 [c]	1393.39[c]
α	4.5[a]	1.38299	164.367	1.383192[c]	164.111[c]
U	0.427919	1.016418	0.068968	1.018163	0.0696635
$\bar{\omega}$	0.439529	1.068711	0.068982	–	–
IE	0.5	0.903257	0.130096	–	–

The ionization energy values IE are also reported in the last row. All quantities in atomic units.

[a] Exact [15]

[b] Rank-1, this work

[c] From [19]

To our knowledge, no practical prescription to compute the Unsöld energies U_A and U_B is available and they are usually obtained a posteriori from C_6 using Eq. (42). Eqs. (24) and (25) provide an independent definition of effective mean energies $\bar{\omega}_A$, $\bar{\omega}_B$. It might be interesting to compare these values with U_A, U_B obtained from Eq. (42). In Table 6 we report such comparison for H, He and Li atoms; from these data we see that Unsöld energies U and $\bar{\omega}$ values are similar; this is a test of the accuracy of Eq. (39). As already noticed by Norman et al. [36], these Unsöld energies exhibit large variations from atom to atom. A relation between U and the ionization energy IE has also been advocated [36]. However, a comparison of U with IE (computed at FCI level) values reported in the same Table 6 does not suggest any simple relation between these quantities.

To conclude, the rank-1 ansatz provides a simple and accurate formula for the matrix elements required to compute the dispersion constant C_6 Eqs. (21) and (26); lower accuracy is obviously expected for the non-isotropic constants C_6^{LMN} involving differences among matrix elements. Moreover, the rank-1 ansatz also provides a mathematical definition of the effective energies $\bar{\omega}_A, \bar{\omega}_B$ playing the role of Unsöld energies. The practical value of the formulae is limited by a computational cost comparable to that of the full rank solution of the perturbative equation.

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Appendix 1

Consider the function

$$f(x,y) = 3G_3(y)x^2 - 4G_2(y)x + 2G_1(y) \qquad (43)$$

for real values $x > 0,\ y > 0$. The vanishing $f(x,y) = 0$ results in a 2nd degree equation in x. Since $G_k(y) > 0$, $f(x,y)$ can vanish only if the discriminant

$$\Delta = -24[G_1(y)G_3(y) - (G_2(y))^2] - 8(G_2(y))^2 \qquad (44)$$

is greater than zero. But $G_1(y)G_3(y) > (G_2(y))^2$ by the Cauchy–Schwarz inequality, and therefore $\Delta < 0$.

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