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REGULAR ARTICLE

A numerical method for computing dispersion constants

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Abstract We reformulate and discuss a previously proposed variational numerical technique for the computation of dispersion coefficients. The method extends the Full CI idea to the perturbation equation for the intermolecular interaction, by expanding the perturbative solution in a small number of tensor products of suitably chosen Full CI vectors. Some new expansion vectors are proposed and their convergence properties are tested by performing computations on HF and H_2O. Last, a natural state analysis of the solution is performed via an orthogonal transformation of the original expansion vectors and it is found that a single couple of natural states strongly dominates the expansion.

1 Introduction

The dispersion interaction of two atoms or molecules at large distance can be computed by perturbation theory according to the classical treatment of London [1, 2], see [3, 4] for an exaustive bibliography. In the context of ab initio calculations, the standard approach is via numerical quadrature of the Casimir-Polder integral of the imaginary frequency polarizabilities [5, 6]. In this paper we review and discuss a numerical variational technique we have used in the last years, and present some new results.

We consider two neutral atoms or molecules at large distance interacting via Coulomb forces, expand the Coulomb A–B interaction in multipoles and, for sake of simplicity, consider only the dipole-dipole dispersion contribution. One has to solve a first order perturbative equation in the tensor product space of the two molecules A, B:

$$\begin{aligned}&\left[(\hat{H}^A - E_0^A) + (\hat{H}^B - E_0^B)\right]\Phi_{1ab}^{AB}\\ &\quad = \left(E_{1a}^A - \hat{\mu}_a^A\right)\Phi_0^A\left(E_{1b}^B - \hat{\mu}_b^B\right)\Phi_0^B \qquad (1)\end{aligned}$$

where, for each molecule, $\hat{H}$, E_0, Φ_0, $\hat{\mu}$ denote the hamiltonian operator, the ground state energy, the ground state wavefunction and the dipole operator, respectively. Different cartesian components of the latter are labelled by indexes a, b, ... The quantities E_{1a}^A, E_{1b}^B are the first order perturbative corrections due to $\hat{\mu}_a^A$, $\hat{\mu}_b^B$, respectively: $E_{1x}^A = \langle\Phi_0^A|\hat{\mu}_x^A|\Phi_0^A\rangle$.

The solution Φ_{1ab}^{AB} of Eq. 1 determines the dispersion contribution to the first order perturbative correction to the zeroth order wavefunction $\Phi_0^A\Phi_0^B$ of the interacting molecules, the other contributions being the induction terms, not considered here. Several formal solutions to Eq. 1 are known; here we quote the following:

- sum-over-states expansion of the solution (London):

$$\Phi_{1ab}^{AB} = \sum_{i>0,\, j>0} \frac{\langle i^A|\mu_a^A|0^A\rangle\langle j^B|\mu_b^B|0^B\rangle}{E_i^A - E_0^A + E_j^B - E_0^B}\,|i^A\rangle|j^B\rangle \qquad (2)$$

where $|i\rangle$, $|j\rangle$ denote eigenvectors of the interacting molecules. The sum excludes the ground state eigenvectors of both molecules and this implies a kind of 'strong orthogonality' of Φ_{1ab}^{AB} to both Φ_0^A and Φ_0^B; see Appendix 1 for details.

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- Casimir-Polder integral representation:

$$\Phi^{AB}_{1ab} = \frac{2}{\pi}\int_0^{+\infty} \frac{(\hat{H}^A - E^A_0)}{(\hat{H}^A - E^A_0)^2 + \omega^2}(E^A_1 - \hat{\mu}^A_a)\Phi^A_0 \times \frac{(\hat{H}^B - E^B_0)}{(\hat{H}^B - E^B_0)^2 + \omega^2}(E^B_1 - \hat{\mu}^B_b)\Phi^B_0 \;\mathrm{d}\omega \tag{3}$$

- Laplace-type integral representation:

$$\Phi^{AB}_{1ab} = -\int_0^{+\infty} e^{-t(\hat{H}^A - E^A_0)}(E^A_1 - \hat{\mu}^A_a)\Phi^A_0 \times e^{-t(\hat{H}^B - E^B_0)}(E^B_1 - \hat{\mu}^B_b)\Phi^B_0 \;\mathrm{d}t \tag{4}$$

as it can be verified by direct substitution. The convergence of the integral is ensured because $\hat{H} - E_0 > 0$ for both molecules when in the ground states.

In this paper we discuss a numerical method of solution of Eq. 1, involving an expansion of Φ^{AB}_{1ab} in products of Slater determinants of the two separate molecules. Once Φ^{AB}_{1ab} is available, the dispersion energy can be obtained by computing matrix elements of the form:

$$\langle ab|ab\rangle_{\otimes} = \left\langle (E^A_1 - \hat{\mu}^A_a)\Phi^A_0 (E^B_1 - \hat{\mu}^B_b)\Phi^B_0 | \Phi^{AB}_{1ab}\right\rangle_{\otimes} \tag{5}$$

where the bra-ket notation $\langle|\rangle_{\otimes}$ in Eq. 5 denotes integration over the configuration space of both molecules.

We remind that the standard Casimir-Polder evaluation of the dispersion coefficients is performed via the equation:

$$\langle ab|ab\rangle_{\otimes} = \frac{1}{2\pi}\int_0^{+\infty} \alpha_{aa}(i\omega)\alpha_{bb}(i\omega)\;\mathrm{d}\omega \tag{6}$$

involving the polarizabilities α at imaginary frequencies:

$$\alpha_{aa}(i\omega) = 2\sum_{i>0} \frac{\langle 0|\mu_a|i\rangle\langle i|\mu_a|0\rangle(E_i - E_0)}{(E_i - E_0)^2 + \omega^2} \tag{7}$$

where now $\langle\,|\,\rangle$ refers to a single molecule space. The integral in Eq. 6 is usually evaluated by numerical quadrature [5, 6] by computing values of $\alpha(i\omega)$ at integration points $i\omega_1$, $i\omega_2$, …. In a CI context, the computation of $\alpha(i\omega)$ is performed via the solution of systems of linear equations, see, e.g. [7]. An interesting alternative is the analytical integration of suitable functions interpolating $\alpha(i\omega)$ in $[0,\infty)$, [8, 9].

2 Outline of the method

In this section we reformulate the method originally proposed in [10]. In the Full CI approach we expand the wavefunctions Φ^A_0, Φ^B_0 of the interacting molecules A, B in Slater determinants S^A_k, S^B_l and compute the ground state energies E^A_0, E^B_0. These Slater determinants define the Full CI spaces FCI^A, FCI^B; both spaces have huge dimensionality, several millions, even some billions [11]. We now expand the solution of Eq. 1 in products of the same Slater det.s of FCI^A, FCI^B spaces respectively as:

$$\Phi^{AB}_{1ab} \approx \sum_{k,l} X_{k,l}\, S^A_k S^B_l, \quad S \;=\; \text{Slater det.} \tag{8}$$

We arrange the expansion coefficients $X_{k,l}$ as a rectangular matrix, where the row index k and the column index l refer to molecules A and B, respectively. We also expand the r.h.s. of Eq. 1 in the Slater determinant basis:

$$(E^A_1 - \hat{\mu}^A_a)\Phi^A_0 \approx \sum_k q^A_k S^A_k \tag{9}$$

$$(E^B_1 - \hat{\mu}^B_b)\Phi^B_0 \approx \sum_l q^B_l S^B_l \tag{10}$$

The first order equation (1) can be recast in the form:

$$\mathbf{X}(\mathbf{H}^A - E^A_0) + (\mathbf{H}^B - E^B_0)\mathbf{X} + \mathbf{q}^B(\mathbf{q}^A)^T = \mathbf{0} \tag{11}$$

where now $\mathbf{H}^A$, $\mathbf{H}^B$ formally denote Full CI hamiltonian matrices, and E^A_0, E^B_0 the ground state energies. The vectors $\mathbf{q}^{\Theta}$, $\Theta = A$, B are the Full CI representation of $(E^{\Theta}_{1\tau} - \hat{\mu}_{\tau})\Phi^{\Theta}_0$, and they are exactly those required for polarizability computations of the separate molecules. They are computed from the ground state eigenvector and the matrix of the dipole operator [7].

Equation 11 is a Sylvester equation; the particular case $(\mathbf{H}^B - E^B_0) = (\mathbf{H}^A - E^A_0)$ is called Lyapunov equation. Such equations have been extensively studied in the field of optimal control theory, see [12]. Equation 11 is the projection of Eq. 1 in the tensor product space FCI$^A \otimes$ FCI^B and, needless to say, its exact solution will coincide with the exact solution of Eq. 1 only in the limit of complete and therefore infinite Full CI expansion for both molecules.

Our approach is to look for a variational solution of Eq. 11 that can be efficiently implemented in a computer code and to provide error bounds for the computed matrix elements. It is immediately realized that the number of elements $X_{k,l}$ is exceedingly large, being the product of the dimensionalities of two Full CI spaces. However we can get a manageable representation of $\mathbf{X}$ by introducing suitable expansion vectors in Full CI spaces of A and B, respectively: $\mathbf{z}^A_i$, $i = 1, \ldots, k_A$, $\mathbf{z}^B_j$, $j = 1, \ldots, k_B$ such that the huge array $\mathbf{X}$ can be approximated by a *small number* of products of the type:

$$\mathbf{X} = \sum_{i,j} c_{i,j}\mathbf{z}^B_j(\mathbf{z}^A_i)^T = \mathbf{Z}^B\mathbf{c}(\mathbf{Z}^A)^T \tag{12}$$

where the vectors $\mathbf{z}^A_i$, $\mathbf{z}^B_j$ are orthogonal to the ground state Full CI eigenvector of molecule A and B, and the coefficients $c_{i,j}$ are to be determined by a variational criterion. Since the number of products in Eq. 12 determines the rank of the matrix $\mathbf{X}$, the latter can be called a low-rank solution. It is convenient to gather the expansion vectors as columns of rectangular matrices $\mathbf{Z}^A$, $\mathbf{Z}^B$, respectively. These will be *tall* matrices, their number of rows being the dimensionality of the Full CI space. Provided we can find effective expansion vectors, the perturbative problem in the huge tensor product space $\mathrm{FCI}^A \otimes \mathrm{FCI}^B$ requires the handling of Full CI vectors only and can therefore be implemented in much the same way as Full CI for single molecules. Abelian symmetry of the interacting molecules is also easily implemented. The Full CI space of each molecule A, B, is the direct sum of subspaces $\mathrm{FCI}^{\Theta}_{\tau}$ where $\Theta = A, B$ and τ labels spacial symmetries. Equation 11 is trivially projected in the product space $\mathrm{FCI}^A_a \otimes \mathrm{FCI}^B_b$; therefore the expansion vectors for each molecule are actually symmetry adapted and should be given a symmetry label, $\mathbf{z}^{\Theta}_{i\tau}$. For sake of simplicity, in the following we omit the symmetry indexes.

As discussed in [10], the coefficients $c_{i,j}$ can be determined either by Hylleraas' variational principle or by minimization of the residual norm in the tensor product space $\mathrm{FCI}^A \otimes \mathrm{FCI}^B$.

The final equation for the optimal coefficient matrix $\mathbf{c}$ by Hylleraas' principle is a *small size* $k_A \times k_B$ generalized reduced Sylvester equation [10]:

$$\mathbf{S}^B\mathbf{c}\mathbf{H}^{1A} + \mathbf{H}^{1B}\mathbf{c}\mathbf{S}^A + \mathbf{b}^{1B}(\mathbf{b}^{1A})^T = 0 \tag{13}$$

where the following *reduced matrices* are involved:

$$\begin{aligned}
&\mathbf{S}^{\Theta} = (\mathbf{Z}^{\Theta})^T\mathbf{Z}^{\Theta},\\
&\mathbf{H}^{1\Theta} = (\mathbf{Z}^{\Theta})^T(\hat{H}^{\Theta} - E_0^{\Theta})\mathbf{Z}^{\Theta},\\
&\mathbf{b}^{1\Theta} = (\mathbf{Z}^{\Theta})^T)\mathbf{q}^{\Theta},\\
&\Theta = A, B
\end{aligned}$$

for each molecule, respectively. A somewhat more complicated, but similar, equation is obtained by the minimal norm criterion [10]. As concerns the computer implementation, we found convenient to work with orthonormalized expansion vectors $(\mathbf{Z}^{\Theta})^T\mathbf{Z}^{\Theta} = \mathbf{I}^{\Theta}$; therefore matrices $\mathbf{S}^A$, $\mathbf{S}^B$ disappear from Eq. 13. The reduced hamiltonian matrices $\mathbf{H}^{1\Theta}$ in Eq. 13 are computed using the standard technology of direct CI.

The matrix equation (13) is easily solved by transforming it in a system of $k_A\, k_B$ linear equations (small × small!). The time consuming part of the procedure is the computation of the expansion vectors; the reduced matrices and Eq. 13 require a comparatively negligible time.

The matrix elements needed for the computation of dispersion constants are obtained from the Full CI version of Eq. 5:

$$\begin{aligned}
\langle {\mu_a}^A {\mu_b}^B | {\mu_a}^A {\mu_b}^B \rangle_{\otimes} &= Tr\{\mathbf{X}^T\mathbf{q}^B(\mathbf{q}^A)^T\}\\
&= Tr\{(\mathbf{b}^A)^T\mathbf{c}^T\mathbf{b}^B\}
\end{aligned} \tag{14}$$

We remark that the matrices appearing in Eq. 13 are obtained from calculations on individual molecules and therefore can be used to compute several different interactions. Once we have chosen the expansion vectors $\mathbf{Z}^{\mathbf{A}}$, $\mathbf{Z}^{\mathbf{B}}$ for two molecules A, B, we compute for each molecule a set of reduced matrices according to the symmetries, and we can set up the reduced Sylvester equations (11) for all the different interactions $A_x - A_x$, $A_x - A_y$, $A_x - A_z$, $\ldots, A_x - B_x$, $\ldots, B_z - B_z$.

As a further remark, if one diagonalizes the reduced hamiltonian matrices appearing in Eq. 13

$$\begin{aligned}
&(\mathbf{U}^{\Theta})^T\mathbf{H}^{1\Theta}\mathbf{U}^{\Theta} = \mathrm{Diag}(\epsilon_1^{\Theta}, \epsilon_1^{\Theta}, \ldots)\\
&(\mathbf{U}^{\Theta})^T\mathbf{S}^{1\Theta}\mathbf{U}^{\Theta} = \mathbf{I}^{\Theta} = \mathrm{Diag}(1, 1, \ldots)
\end{aligned} \tag{15}$$

one gets a *pseudo spectrum* of excitation energies ε_1^{Θ}, ε_1^{Θ}, …. The present method of solution is actually mathematically equivalent to the London Eq. 2 using as expansion pseudostates the Full CI vectors provided by the columns of the matrices $\mathbf{U}^{\Theta}\mathbf{Z}^{\Theta}$.

2.1 Convergence check and error bounds

The accuracy of an approximate solution $\mathbf{X}$, and, consequently, the convergence of the method is measured by the norm of the residual of Eq. 11, given by:

$$\mathbf{R} = \mathbf{X}(\mathbf{H}^A - E_0^A) + (\mathbf{H}^B - E_0^B)\mathbf{X} + \mathbf{q}^B(\mathbf{q}^A)^T \tag{16}$$

$$\|\mathbf{R}\| = \sqrt{Tr\{\mathbf{R}^T\mathbf{R}\}} \tag{17}$$

The norm of the residual cannot be computed by straightforward summation of the squares if its individual components because of the huge number of them, given by the product of the dimensions of the Full CI spaces of the interacting molecules. However, as shown in [10], for an $\mathbf{X}$ given by Eq. 12 and orthonormal expansion sets $\mathbf{Z}^A$, $\mathbf{Z}^B$ one has:

$$\begin{aligned}
\|\mathbf{R}\|^2 = {} & (\mathbf{b}^B)^T\mathbf{b}^B(\mathbf{b}^A)^T\mathbf{b}^A + 2Tr\{(\mathbf{b}^{2B})^T\mathbf{c}\,\mathbf{b}^{1A}\}\\
& + 2Tr\{(\mathbf{b}^{1B})^T\mathbf{c}\,\mathbf{b}^{2A}\} + Tr\{\mathbf{c}^T\,\mathbf{H}^{2B}\,\mathbf{c}\}\\
& + Tr\{\mathbf{c}\,\mathbf{H}^{2A}\,\mathbf{c}^T\} + 2Tr\{(\mathbf{H}^{1B})^T\mathbf{c}\,\mathbf{H}^{1A}\mathbf{c}^T\}
\end{aligned} \tag{18}$$

where

$$\begin{aligned}
&\mathbf{H}^{2\Theta} = (\mathbf{Z}^{\Theta})^T(\hat{H}^{\Theta} - E_0^{\Theta})^2\mathbf{Z}^{\Theta},\\
&\mathbf{b}^{2\Theta} = (\mathbf{Z}^{\Theta})^T(\hat{H}^{\Theta} - E_0^{\Theta})\mathbf{q}^{\Theta},\\
&\Theta = A, B
\end{aligned}$$

The additional matrices appearing in Eq. 18 are computed from the same vectors needed for the matrices in Eq. 13 and the additional computer time required is negligible. It should be pointed out that the quantities in Eq. 18 have mixed signs and this introduces some loss of accuracy in the computation of $\|\mathbf{R}\|^2$. We empirically assumed this loss to be of the order $\approx 10^{-12}$ for our double precision computations with a machine precision of 10^{-14}.

As concerns the accuracy of the matrix elements computed by Eq. 14, when $\mathbf{X}$ is obtained from Hylleraas' variational principle, we get lower bounds to 'diagonal' matrix elements:

$$\langle {\mu_a}^A {\mu_b}^B | {\mu_a}^A {\mu_b}^B \rangle_{\otimes} \leq M_{fc} \tag{19}$$

where M_{fc} represents the exact value for a fully converged solution $\mathbf{X}_{fc}$ with a residual norm strictly vanishing. Lower bound formulae to second order perturbative corrections [13] applied to Eq. 11 provide upper bounds to the same matrix elements:

$$M_{fc} \leq \langle {\mu_a}^A {\mu_b}^B | {\mu_a}^A {\mu_b}^B \rangle_{\otimes} + \frac{\|\mathbf{R}\|^2}{E_{\mathrm{exc}} - E_0} \tag{20}$$

where E_{exc} is the first excited level (of appropriate symmetry) of the joint non-interacting system $A{-}B$. Here we have one of the advantages of the present method over the standard Casimir-Polder procedure, where the accuracy of the numerical integration can hardly be checked.

2.2 Choice of the expansion sets

In this section we show how to get effective vectors to expand the solution of Eq. 11. It is understood that the vectors, once generated with the prescriptions here described, are always orthonormalized and also orthogonalized to the ground state of the molecule, as implied by Eq. 2; see Appendix 1 for details.

In our past computations [14, 15], we have used the following two sets. The first one was suggested by the Casimir-Polder procedure. To compute the polarizability at an imaginary frequency by Full CI one has to solve a set of first order perturbative equations of the type:

$$(\mathbf{H}^{\Theta} - E_0^{\Theta} + i\omega)\mathbf{z}^{\Theta} = \mathbf{q}^{\Theta}, \quad \Theta = A, B \tag{21}$$

The Full CI solutions obtained in this way for $\omega = \omega_1$, ω_2, … are natural choices for the expansion vectors $\mathbf{z}_j^A$, $j = 1, \ldots, k_A$, $\mathbf{z}_j^B$, $j = 1, \ldots, k_B$. As already pointed out in [10], the numerical Casimir Polder with integration points ω_k and weights w_k is a particular case of Eq. 8 where the expansion set is given by the real parts of the solutions of Eq. 21 and assuming a diagonal matrix of coefficients: $c_{ik} = \frac{w_k}{2\pi}\delta_{ik}$. Therefore the coefficients are not variationally optimized. In this connection we should also remind that a perturbative solution at imaginary frequency is a complex Full CI vector so its real and imaginary parts provide two independent expansion vectors that can be included in the basis [10].

A second choice was suggested by the Cauchy moment expansion of the polarizability in powers of the frequency ω. A CI computation of the Cauchy moments implies the solution of PT-like equations in FCI$_A$ and FCI$_B$ spaces at $\omega = 0$:

$$(\mathbf{H} - E_0)\mathbf{z}_n = \mathbf{z}_{n-1}, \quad n = 1, 2, \ldots \quad \text{and} \quad \mathbf{z}_0 = \mathbf{q} \tag{22}$$

In the present study we consider some other possibilities. Expanding the exponential of Eq. 4 in McLaurin series suggests the set:

$$(\mathbf{H} - E_0)^n \mathbf{q} = \mathbf{z}_n, \quad n = 1, 2, \ldots \tag{23}$$

We call this the *power* set, P. The generation of the vectors of Eq. 23 is not costly in computer time, but on the other hand the convergence is rather slow. Therefore this set requires a large amount of disk space to keep all the vectors needed for a satisfactory convergence and this is unconvenient when dealing with large Full CI expansions.

Another set is here investigated. It is suggested by the following arguments. By assuming a single product or rank-1 expansion of the solution $\mathbf{X} = \mathbf{z}^A c_1 \mathbf{z}^B$ and using the Hylleraas' variational principle it can be shown that the optimal vectors are given by the solutions of the following equations [16]:

$$\begin{aligned} (\mathbf{H}^A - E_0^A + \omega_B)\mathbf{z}^A &= \mathbf{q}^A \\ (\mathbf{H}^B - E_0^B + \omega_A)\mathbf{z}^B &= \mathbf{q}^B \end{aligned} \tag{24}$$

where ω_A, ω_B are real, positive quantities to be determined by a nonlinear minimization procedure. The approximation provided by the simple product is surprisingly good (>99%), but the determination of the ω's is very time consuming, so the method is not practical. This suggests that a good expansion set for the solution Eq. 12 should include solutions of Eq. 24 at suitably chosen values ω_1,ω_2, …. Since a variational choice of such values of ω is unfeasible, we considered the following procedure. We perform a preliminary cheap computation with a small power set (23). The resulting approximate solution is analysed in natural states as described in Sect. 4 and from them we get the values of ω_k as the excitation energies of the first natural states as detailed in Eq. 35. We call this the solution set S. As a cheaper variant we can use the first excitation energies $\omega_1 < \omega_2 < \cdots$ obtained from a small Lanczos iteration starting from $\mathbf{q}^B$.

Since these values are certainly non-optimal, we mimic the possibility of adjusting the values of the ω's by also including the derivatives of $\mathbf{z}^A(\omega)$ w.r.t. ω. By using the formula for the n-th derivative of a product one gets from Eq. 24:

$$(\mathbf{H} - E_0 + \omega)\frac{d^n \mathbf{z}^A}{\mathrm{d}\omega^n} + n\frac{d^{n-1}\mathbf{z}^A}{\mathrm{d}\omega^{n-1}} = \mathbf{0} \tag{25}$$

Therefore the expansion vectors $\mathbf{z}_{k,n}^A$ are defined by the following equation:

$$(\mathbf{H} - E_0 + \omega_k)\mathbf{z}^A_{k,n} = \mathbf{z}^A_{k,n-1},$$
$$k = 1, 2, \ldots, \; n = 1, 2, \ldots, \text{ and } \mathbf{z}^A_{k,0} = \mathbf{q}^A \qquad (26)$$

where k labels a value of ω and n a derivative order. As concerns the computational cost, each vector $\mathbf{z}^A_{k,n}$ of Eq. 26 requires roughly one half of the computer time needed by a single value of polarizability at imaginary frequency. Indeed the system of linear equations (26) is well conditioned because ω_k is greater than the first excitation energy of $\mathbf{H}$, and the conjugate gradient converges fast.

3 Test calculations

The properties of the method with the new expansion set are here illustrated by test Full CI calculations on HF and water. We choosed the Z3 AO bases of Benkova et al. [17] because they are specially designed for polarizability calculations and, due to their reduced size, allow for reasonable Full CI expansions.

As far as HF is concerned, the details of the Full CI calculation are reported in Table 1. Basis set and geometry are the same used in [16]: the bond length is 1.8012 bohr, the AO basis is the 24 CGTO Z3 6s3p/3s1p of Benkova et al. [17], and the $1s^2$ of fluorine is frozen. The dimension of the Full CI space is about 20 million Slater determinants in each symmetry class (C_{2v}).

As concerns the Full CI calculations on water (Table 2), we optimized the geometry at RCCSD(T)/VDZ level and got an O–H bond length of 1.889 bohr and an HOH angle of 104.099°. The symmetry group is C_{2v} with the y axis perpendicular to the molecular plane and the z axis coincident with C_2. After a SCF calculation on the molecule, we froze the $1s^2$ pair of oxygen so our Full CI involves 8 correlated electrons in 29 orbitals and about 141 million Slater determinants per symmetry class.

The expansion sets for the dispersive computation include six vectors of the type:

$$\mathbf{z}_i = (\mathbf{H} - E_0 + \omega_k)^{-i}\mathbf{q}, \quad k = 1, 2, \; i = 1, 2, 3 \qquad (27)$$

for each symmetry of both molecules; the values of ω_k are given in Table 3. According to the remarks given in Sect. 2.2, such a calculation with six vectors of type (27) requires roughly the computer time needed by a 3–4 points Casimir-Polder procedure, while the standard number of integration points is 8 to 16 imaginary frequencies [5, 6].

Table 1 Details of the Full CI calculation on HF

State	N_{FCI}	E	ΔE
$X^1\Sigma^+$	19,602,925	−100.18068391	0.0
$1^1\Sigma^+$	19,602,925	−99.64196314	0.53872077
$1^1\Pi$	19,602,700	−99.79891313	0.38177078
Dipole	Polarizability, a_0^3		
0.680820	$\alpha_\perp = 5.267232$, $\alpha_\parallel = 6.141682$		

N_{FCI} is the number of Slater determinants of the Full CI expansion, E is the total energy and ΔE the transition energy in hartrees

Table 2 Results of the Full CI calculation for water

State	N_{FCI}	E	ΔE
1^1A_1	141,140,491	−76.18750732	0.0
2^1A_1	141,140,491	−75.83391284	0.35359448
1^1B_1	141,126,410	−75.76699190	0.42051542
1^1B_2	140,924,450	−75.92135832	0.26614900
Dipole	Polarizability, a_0^3		
0.308341	$\alpha_{xx} = 10.676927$	$\alpha_{yy} = 9.982857$	$\alpha_{zz} = 9.890958$

N_{FCI} is the number of Slater determinants of the Full CI expansion, E is the total energy and ΔE the transition energy in hartrees. The y axis is perpendicular to the molecular plane and the z axis coincides with C_2

Table 3 Values of ω_k (hartrees) used to compute the expansion vectors for HF and H_2O

Molecule	Symmetry	ω_1	ω_2
HF	$\parallel$	0.88016020	1.18381439
HF	$\perp$	0.91737303	0.86934192
H_2O	x	0.70660563	1.04742176
H_2O	$y, \perp$	0.67737888	0.71488351
H_2O	$z = C_2$	0.69966900	0.90364375

Results of the computation of dispersive matrix elements for HF and H_2O are reported in Table 4. From these values we computed the dispersion coefficients C_6^{00000} using the formulae given in Appendix 2 and the dimensionless anisotropy factors computed according to [18]:

$$\gamma_6^{ijklm} = \frac{C_6^{ijklm}}{C_6^{00000}} \qquad (28)$$

Given the error bounds reported in Table 4, we get an accuracy $\leq 0.5 \times 10^{-7}$ on the values reported in Table 5. The comparison with literature values shows satisfactory agreement for the isotropic coefficient C_6^{00000} and discrepancies for the anisotropic factors. In this connection it should be reminded that our Full CI computations are performed using small size AO basis sets, not including as many polarization functions as the larger sets used in [18–20].

4 Natural states analysis of the solution

Thirty years ago Kutzelnigg and Maeder [21–24] proposed a 'natural expansion' of the perturbative solution Φ^{AB}_{1ab} of Eq. 1 of the form:

Table 4 Matrix elements for HF−HF, HF−H_2O, and HF−H_2O dispersion interactions and the value of $\|\mathbf{R}\|^2/(E_{\mathrm{exc}}-E_0)$ (in parentheses), see Eq. 20

	$HF_{\parallel}$	$HF_{\perp}$	$H_2O_{\perp}$	H_2O_x	H_2O_z
$HF_{\parallel}$	3.89308008 (3.9E-11)	3.36792130 (2.8E-09)	5.36943220 (8.7E-08)	6.053566848 (0.79E-10)	5.48582529 (6.7E-12)
$HF_{\perp}$		2.91487260 (1.1E-08)	4.63565401 (3.4E-07)	5.226619927 (0.16E-08)	4.73694259 (5.5E-08)
$H_2O_{\perp}$			7.51022647 (2.2E-08)	8.449315606 (0.41E-08)	7.66018202 (6.4E-08)
H_2O_x				9.513048175 (0.53E-10)	8.621328685 (0.12E-09)
H_2O_z					7.81508267 (2.0E-09)

The H_2O molecule lies in the xz plane, and the z axis coincides with C_2. All quantities are in a.u.

Table 5 Van der Waals dispersion coefficients C_6^{00000} (a.u.) and dimensionless anisotropy factors γ_6^{ijklm} (see Eq. 28)

	H_2O-H_2O	HF−H_2O	HF−HF	References
C_6^{00000}	49.5333400	30.7381719	19.3495040	This work
γ_6^{20002}	−0.0302491	0.1120093	0.1102659	This work
γ_6^{00202}	−0.0302491	−0.0297803	0.1102659	This work
γ_6^{22002}	0.0546242	0	0	This work
γ_6^{00222}	0.0546242	0.0554190	0	This work
γ_6^{22224}	0.0081206	0	0	This work
C_6^{00000}	48.79	31.63	20.75	MBPT [18]
γ_6^{20002}	0.006	0.173		MBPT [18]
γ_6^{00202}			0.169	MBPT [18]
γ_6^{00222}	0.130	0.130		MBPT [18]
C_6^{00000}	46.433			MBPT [19]
γ_6^{22002}	0.0647			MBPT [19]
γ_6^{22224}	0.0112			MBPT [19]
C_6^{00000}	43.17			LB94 [20]
γ_6^{22002}	0.077			LB94 [20]
γ_6^{22224}	0.016			LB94 [20]

$$\Phi_{1ab}^{AB} = \sum_k \phi_k^A \phi_k^B \tag{29}$$

where to each natural state ϕ_k^A of molecule A corresponds an associated natural state ϕ_k^B of molecule B. Kutzelnigg and Maeder argued that such an expansion should have good convergence properties, and this was indeed verified in a number of simple cases [21]. The Ansatz (1) can be investigated at the Full CI level as follows. Given a converged solution to Eq. 11, we can reduce to diagonal form the matrix $\mathbf{c}$ of the coefficients via a singular value decomposition (SVD) performed with two orthogonal matrices: $\mathbf{U}^A$, $\mathbf{U}^B$:

$$\mathbf{c} = \mathbf{U}^B \boldsymbol{\Lambda} (\mathbf{U}^A)^T \quad \boldsymbol{\Lambda} = \mathrm{Diag}(\lambda_1, \lambda_2, \ldots) \tag{30}$$

$$\mathbf{X} = \sum_k [\mathbf{Z}^B \mathbf{U}^B]_k \lambda_k [\mathbf{Z}^A \mathbf{U}^A]_k^T \quad k = 1, \ldots, \mathrm{rank}(\mathbf{c}) \tag{31}$$

where we have used the notation $[\mathbf{M}]_k$ for the column k of matrix $\mathbf{M}$. The couple of corresponding vectors $\mathbf{y}_k^A$, $\mathbf{y}_k^B$ given by

$$y_{ik}^{\Theta} = \sum_j Z_{i,j}^{\Theta} U_{j,k}^{\Theta}, \quad \Theta = A, B \tag{32}$$

associated to each singular value λ_k provide the expansion coefficients of the natural states in Slater determinants:

$$\phi_k^{\Theta} = \sqrt{\lambda_k} \sum_l S_i^{\Theta} y_{ik}^{\Theta}, \ \Theta = A, B \tag{33}$$

It is found that the singular values $\lambda_1 \geq \lambda_2 \geq, \ldots, \lambda_k, \ldots, \geq 0$ decay very rapidly with the index k in such a way that *one couple strongly dominates* the expansion, i.e. to a very good approximation the solution $\mathbf{X}$ is given by a product of one vector $\in \mathrm{FCI}_A$ by a single vector $\in \mathrm{FCI}_B$. A typical result is shown in Table 6. This behaviour has been observed for Lyapunov equations in control theory [25], and it is still the subject of investigation in that field. We notice that by retaining only the dominating term in expansion (29) we get a rank-1 approximation to the solution $\mathbf{X}$ similar to that discussed in [16]. The difference between these two rank-1 approximations lies in the approximation criteria: the present one minimizes the (euclidean) distance from the solution $\mathbf{X}$, while that of [16] fulfills Hylleraas' variational principle and minimizes the second order perturbative correction i.e. it maximizes the dispersion energy.

In the same Table 6 we also report the contribution D_k of each natural state $\mathbf{y}_k$ to the dispersion matrix element, and the associated excitation energy ω_k. The former is obtained by combining Eqs. 14 and 30:

$$\langle {\mu_1}^A {\mu_2}^B | {\mu_1}^A {\mu_2}^B \rangle = \sum_k (\mathbf{y}_k^A)^T \lambda_k \mathbf{y}_k^B$$
$$= \sum_k D_k \quad k = 1, \ldots, \mathrm{rank}(\mathbf{c}) \tag{34}$$

As concerns the associated excitation energy ω_k, one has:

$$\omega_k^{\Theta} = \frac{(\mathbf{y}_k)^T (\mathbf{H}^{\Theta} - E_0^{\Theta}) \mathbf{y}_k}{(\mathbf{y}_k)^T \mathbf{y}_k} \tag{35}$$

As previously stated in Sect. 2.2, values of ω computed with a low-quality 'power' expansion set are used to define the expansion set S.

Table 6 Example of natural analysis of the solution of Eq. 13 for $H_2O_y - H_2O_y$ interaction, the y axis being perpendicular to the molecular plane

k	λ_k	%	D_k	%	ω_k
1	0.69218016E+00	94.193	0.74847645E+01	99.661	0.67722183
2	0.39445869E-01	5.368	0.25228948E-01	0.336	0.70288972
3	0.30824709E-02	0.419	0.23229712E-03	0.003	1.0598318
4	0.14169250E-03	0.019	0.74153318E-06	0.000	1.6011351
5	0.64826435E-05	0.001	0.13445667E-08	0.000	1.3869767
6	0.12495012E-06	0.000	0.14064981E-11	0.000	3.9053223
$\sum_k$	0.73485680	100	7.51022647	100	–

Singular values λ_k, contributions D_k to the dispersion matrix element $\langle YY|YY\rangle$, and excitation energies ω_k are given in a.u.

5 Conclusion

The method discussed in this paper is the natural extension of Full CI to the domain of intermolecular interactions and, as such, it shares the virtues and limitations of Full CI.

The method here discussed has the following advantages: (1) it provides variational upper and lower bounds to the intermolecular matrix elements and therefore it allows for convergence control; (2) it is computationally efficient and provides faster convergence w.r.t. numerical Casimir-Polder.

On the other hand, the method is at the moment implemented in a Full CI code, although all its mathematical structure is not limited to Full CI. This means that it can be used to compute benchmark values for small molecules and/or with small AO sets. As concerns the comparison with Casimir-Polder, it should be remarked that the latter is not limited to CI contexts and this allows the use of much larger AO sets on much larger molecules.

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Appendix 1

Strictly speaking, Eq. 1 has an infinity of solutions, since to any given solution Φ^{AB}_{1ab} we can add products of the type $\Phi^A_0 f^B$ and $g^A\,\Phi^B_0$, where f^B and g^A are arbitrary functions, and get another solution. The dispersion solution is characterized by a kind of strong orthogonality to the ground state eigenvectors of molecule A and B, as clearly shown by the London sum-over-states representation given in Eq. 2:

$$\int_A \Phi^{AB}_{1ab}\Phi^A_0\, dV_A = \int_B \Phi^{AB}_{1ab}\Phi^B_0\, dV_B = 0$$

Equivalently, we can define Φ^{AB}_{1ab} to be the solution of minimal norm of Eq. 1. As far as Eq. 11 is concerned, one has the conditions:

$$\mathbf{v}^A_0\mathbf{X} = \mathbf{0}^B = \mathbf{0}, \quad \mathbf{X}(\mathbf{v}^B_0)^T = (\mathbf{0}^A)^T$$

where $\mathbf{v}^A_0$, $\mathbf{v}^B_0$ are the Full CI ground state eigenvectors of molecule A, B, respectively, and $\mathbf{0}^A$, $\mathbf{0}^B$ are zero vectors. Consequently, the expansion vectors should fulfill the orthogonality requirements:

$$(\mathbf{z}^A_i)^T\mathbf{v}^A_0 = (\mathbf{z}^B_j)^T\mathbf{v}^B_0 = 0.$$

Appendix 2

For reader's convenience we report here the explicit formulae used to compute the dispersion coefficients from the cartesian matrix elements:

$$\begin{aligned}
C_6^{00000} =& \frac{2}{3}[\langle xx|xx\rangle_\otimes + \langle xy|xy\rangle_\otimes + \langle xz|xz\rangle_\otimes \\
&+\langle yx|yx\rangle_\otimes + \langle yy|yy\rangle_\otimes + \langle yz|yz\rangle_\otimes \\
&+\langle zx|zx\rangle_\otimes + \langle zy|zy\rangle_\otimes + \langle zz|zz\rangle_\otimes] \\
C_6^{20002} =& -\frac{\sqrt{5}}{3}[\langle xx|xx\rangle_\otimes + \langle xy|xy\rangle_\otimes + \langle xz|xz\rangle_\otimes \\
&+\langle yx|yx\rangle_\otimes + \langle yy|yy\rangle_\otimes\langle yz|yz\rangle_\otimes \\
&-2(\langle zx|zx\rangle_\otimes + \langle zy|zy\rangle_\otimes + \langle zz|zz\rangle_\otimes)] \\
C_6^{22002} =& \sqrt{\frac{5}{6}}[\langle xx|xx\rangle_\otimes + \langle xy|xy\rangle_\otimes + \langle xz|xz\rangle_\otimes \\
&-(\langle yx|yx\rangle_\otimes + \langle yy|yy\rangle_\otimes + \langle yz|yz\rangle_\otimes)] \\
C_6^{22224} =& \frac{27}{\sqrt{70}}[\langle xx|xx\rangle_\otimes - \langle xy|xy\rangle_\otimes - \langle yx|yx\rangle_\otimes + \langle yy|yy\rangle_\otimes]
\end{aligned}$$

in the notation defined by Eq. 5.

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