

# **A Study of Dispersion Forces with Quantum Monte Carlo: Towards a Continuum Model for Solvation**

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## Abstract

We present a general method to compute dispersion interaction energy that, starting from London’s interpretation, is based on the measure of the electronic electric field fluctuations, evaluated on electronic sampled configurations generated by quantum Monte Carlo. A damped electric field was considered in order to avoid divergence in the variance. Dispersion atom-atom  $C_6$  van der Waals coefficients were computed by coupling electric field fluctuations with static dipole polarizabilities. The dipole polarizability was evaluated at the diffusion Monte Carlo level by studying the response of the system to a constant external electric field. We extended the method to the calculation of the dispersion contribution to the free energy of solvation in the framework of the polarizable continuum model. We performed test calculations on pairs of some atomic systems. We considered He in ground and low lying excited states and Ne in the ground state and obtained a good agreement with literature data. We made also calculations on He, Ne and  $F^-$  in water as solvent. Resulting dispersion contribution to the free energy of solvation show the reliability of the method illustrated here.

## Introduction

The dispersion energy describes the electronic correlation between two distributions due to the simultaneous coupling of mutually induced density fluctuations. This term determines attractive forces that have been recognized for the first time by London<sup>1</sup> who explained in this way the long range attraction between noble gas atoms. The dispersion interactions are an important part of the van der Waals (vdW) forces. In chemistry, these play a significant role in the formation of intermolecular complexes. These forces are much weaker than those which form chemical bonds but are responsible, for example, for the deviation from the ideality of gases and for the existence of the condensed state. All the thermodynamic and transport properties of gases<sup>2</sup> and liquids<sup>3</sup> depend on the characteristics of vdW interaction potentials. For solids these forces determine many properties, notably the equilibrium

geometries, the cohesive energies and the phonon spectra. In biology, similar considerations apply to the weak interactions between different chemical groups in large molecules, typically biopolymers, where they are largely responsible for the equilibrium conformations: an important example is the double helix structure of DNA. Moreover, there is also a wide class of experiments based on modern technology, e.g. molecular beams, molecular laser, shock waves, where the knowledge of intermolecular potentials is very important<sup>4,5</sup>.

The dispersion energy is computed by theoretical methods that go beyond the Hartree-Fock approximation because it is a correlation energy contribution. In this regard, it should be noted that only those methods that include dynamical correlation are appropriate for this purpose, namely those developed within a perturbation theory or those based on very extended configuration interaction schemes. By this way, the interaction potential between two molecules can be efficiently calculated and, after the construction of the relevant potential energy surface (PES), they can be used in a wide range of applications on condensed phases.

One of the most important of these applications is in the theory of solvation to compute the free energy change related to the process in which a molecule (the solute) is introduced in a condensed medium (the solvent)<sup>6,7</sup>. The free energy of solvation is usually decomposed in various contributions, one of which is determined by solute-solvent dispersion energy.<sup>8</sup>

The solvent environment can be considered at different levels of complexity going from the so-called implicit models, in which it is treated as a continuum medium, to the explicit models in which all solvent molecules are explicitly introduced. The methods based on continuum models are widely used because (i) they are preferred from the point of view of the computational cost, (ii) they offer a very good qualitative description of solvation and (iii), nowadays, they have reached a good level of accuracy also for quantitative prediction of solvation properties.

The dispersion contribution to the free energy of solvation can be computed within a polarizable continuum model (PCM) in a variety of approaches. Here, we mention in particular the method of Floris and Tomasi<sup>9,10</sup>, in which a solvent reaction field is not gen-

erated, and that of Amovilli and Mennucci<sup>11,12</sup>, where, instead, such a field is generated and used to optimize the solute wave function. More recently, other interesting semi-empirical approaches have been proposed. Among these approaches, Pomogaeva and Chipman<sup>13,14</sup> uses the electron density of the solute and the density of the solvent, and Marenich et al<sup>15</sup>, combines the static polarizability of the solute and the solvent refractive index. This last approach can also be applied to excited states. Worth of mention is also the method developed by Duignan et al<sup>16,17</sup>, where the method of Floris and Tomasi is extended to higher multipolar expansion terms.

In this work, we first show that quantum Monte Carlo (QMC) is able to provide information to compute dispersion energy coefficients and, with some approximation, dispersion energy potentials without super-molecule calculations, by resorting to the original London's idea of analyzing these interactions in terms of electronic electric field fluctuations. These fluctuations can easily be handled by QMC. Thanks to Unsöld's approximation<sup>18</sup>, which is here generalized to the excited states, we can limit the study to the wave function of the isolated interacting systems. Finally, thanks to Clausius-Mossotti equation for dielectrics, we derive a novel equation for the free energy of solvation that does not contain empirical parameters and that can be applied, in principle, to perform wave function optimization of a solute even in an electronic excited state.

The paper is organized as follows. First, we show in details the theoretical approach used here to compute the dispersion energy with QMC. Second, we present our calculations performed on He, Ne and  $F^-$  in vacuo and in aqueous solution. Finally, in the last section, we draw the conclusion.

## Theory

At very large distance between the two molecules, the dispersion energy is dominated by mutual dipole polarization interactions. Let us then start by considering two atomic systems

in this condition. For two atoms, say A and B, at distance  $R_{AB}$ , the dispersion energy behaves as  $-C_6^{(AB)}/R_{AB}^6$  where  $C_6^{(AB)}$  can be evaluated by London's formula

$$C_6^{(AB)} = \frac{3\alpha_A\alpha_B I_A I_B}{2(I_A + I_B)} \quad (1)$$

in which we use explicitly the static dipole polarizability ( $\alpha$ ) and the ionization potential ( $I$ ) of the two atoms. At this point, in order to rewrite the dispersion coefficient  $C_6^{(AB)}$  in terms of electric field fluctuations, it is useful to make the Unsöld's approximation in the equation which gives the static dipole polarizability from standard Raileigh-Schrödinger perturbation theory, namely

$$\alpha = \frac{2}{3} \sum_{k \neq 0} \frac{\langle 0|\vec{d}|k \rangle \cdot \langle k|\vec{d}|0 \rangle}{\Delta E(0 \rightarrow k)} \approx \frac{2}{3I} \left[ \langle 0|\vec{d}^2|0 \rangle - \langle 0|\vec{d}|0 \rangle \cdot \langle 0|\vec{d}|0 \rangle \right] \quad (2)$$

where

$$\vec{d} = - \sum_{j=1}^{N_{el}} \vec{r}_j \quad (3)$$

is the electronic dipole moment operator, in atomic units, and where the sum runs over all the electronic states  $|k \rangle$  different from the ground state  $|0 \rangle$ ,  $\Delta E(0 \rightarrow k)$  being a transition energy. The Unsöld's approximation made above consists in bringing outside of the sum an average inverse of transition energy, namely  $1/I$ , and by summing all the terms in the numerator which are positive quantities. In computing the latter sum we use the resolution of the identity, namely  $\hat{1} = \sum_k^{all} |k \rangle \langle k|$ . We will use the average transition energy  $I$  coming from this approximation directly in the expression of dispersion coefficient  $C_6^{(AB)}$  above. Moreover, we will extend the Unsöld's approximation to any reference state, not only the ground state, in order to include cases in which the interacting systems are in an

electronic excited state. In these cases,  $I$  will be smaller than that obtained from the ground state reference because an excited state has an energy closer to the ionization threshold. It must be noted also that, for excited states, the Unsöld's approximation subsumes formally also contributions from de-excitations.

Eq(2) allows us to establish a relation with the fluctuations of the electronic electric field of the interacting systems. First of all, we consider the electric field of a dipole ( $\vec{d}_A$ ) positioned at a point A in the space calculated at a point B

$$\vec{\mathcal{E}}_A(\mathbf{R}_B) = \frac{1}{R_{AB}^3} \left[ \frac{3(\vec{d}_A \cdot \vec{R}_{AB})\vec{R}_{AB}}{R_{AB}^2} - \vec{d}_A \right] \quad (4)$$

where  $\vec{R}_{AB} = \vec{R}_B - \vec{R}_A$ . It is convenient to distinguish the longitudinal ( $L$ ) component along the direction of  $\vec{R}_{AB}$  from the two tangential ( $T_1$  and  $T_2$ ) components. These are

$$\mathcal{E}_A^{(L)} = \frac{2d_A^{(L)}}{R_{AB}^3} \quad (5)$$

$$\mathcal{E}_A^{(T_1)} = -\frac{d_A^{(T_1)}}{R_{AB}^3} \quad (6)$$

$$\mathcal{E}_A^{(T_2)} = -\frac{d_A^{(T_2)}}{R_{AB}^3} . \quad (7)$$

The statistical fluctuations of each component is measured by the variance

$$\sigma_{\mathcal{E}}^2 = \langle 0 | \mathcal{E}^2 | 0 \rangle - \langle 0 | \mathcal{E} | 0 \rangle^2 \quad (8)$$

and then, we can rewrite Eq(2) in the form

$$\lim_{R_{AB} \rightarrow \infty} \left[ \frac{1}{4} \sigma_L^2 + \sigma_{T_1}^2 + \sigma_{T_2}^2 \right] R_{AB}^6 = \frac{3}{2} \alpha_A I_A \quad (9)$$

where the variance of the three components of the field have been explicitly used. Turning to the real electronic distribution, instantaneous dipoles are determined by the motion of electrons. Thus, instead of a pure dipolar field we introduce a modified electronic electric field in the form

$$\vec{\mathcal{E}}(\vec{r}) = - \sum_{i=1}^{N_{el}} \frac{(\vec{r} - \vec{r}_i)}{|\vec{r} - \vec{r}_i|^3} f_2(|\vec{r} - \vec{r}_i|) \quad (10)$$

where

$$f_2(r) = 1 - \left( 1 + br + \frac{1}{2} b^2 r^2 \right) e^{-br} \quad (11)$$

is a damping factor that is 1 at infinity and cancels the divergence of the electric field at short distances and where the electronic positions  $\vec{r}_i$  refer to an electronic configuration consistent with a probability distribution given by the square of the wave function. Eq(10) defines a field whose fluctuations evaluated at large distances depend only on fluctuating dipoles, the total electronic charge being constant. For this reason it can be used to compute the vdW  $C_6^{AB}$  coefficients through the limit of Eq(9). The damping factor does not have any effect at large distances being 1 in this regime. This factor is instead very useful in the calculation of the fluctuations at all distances because it leads always to finite variances. This point is important, as we will show below, since at short distances the fluctuations of the field given in Eq(10) can provide further information on dispersion energy variation. In this regard, the damping factor  $f_2(r)$  plays a role similar to that of Tang and Tonnies dispersion coefficient damping factors<sup>19</sup>.

$\mathcal{E}^2$  is a two-electron quantity thus, it brings information about correlation. In this

regard,  $f_2$  has the effect of cancelling the divergence occurring when the field is evaluated at an electron position, but it does not affect the contributions depending on electron-electron distances. These contributions are, in principle, related to dynamical correlation. For this reason, we chose the quantum Monte Carlo method, that uses highly correlated wave functions, to compute the fluctuations of the damped field of Eq.(10). It should be noticed also that the computation of the field fluctuations by means of a stochastic method of integration can be more easily implemented than by using a standard quantum chemistry method.

## The quantum Monte Carlo approach

The quantum Monte Carlo is a stochastic method that can be used to solve the electronic Schrödinger equation. In variational Monte Carlo (VMC) the electronic energy is computed by averaging the so-called local energy on a set of electronic configurations sampled over an optimized  $|\Psi_{VMC}|^2$  distribution,  $\Psi_{VMC}$  being the electronic wave function. In this work, we use a spin-free Jastrow-Slater form written as

$$\Psi_{VMC}(\mathbf{r}_1, \mathbf{r}_2, \dots) = \Phi(\mathbf{r}_1, \mathbf{r}_2, \dots) \mathcal{J}(r_1, r_2, \dots, r_{12}, \dots) \quad (12)$$

where  $\Phi$  is given by

$$\Phi = \sum_K D_K^\uparrow D_K^\downarrow d_K, \quad (13)$$

in which  $D_K^\uparrow$  and  $D_K^\downarrow$  are the Slater determinants written in terms of occupied orbitals of spin-up and spin-down electrons, respectively, and  $d_K$  are the mixing coefficients. The Jastrow correlation factor  $\mathcal{J}$  is the exponential of the sum of three contributions which are functions of electron-nuclear (e-n), electron-electron (e-e) and pure three-body mixed e-e

and e–n distances respectively<sup>20</sup>. This type of function is, in general, compact and is able to introduce a very large fraction of dynamical correlation through the Jastrow factor. Instead, using diffusion Monte Carlo (DMC) in the fixed node approximation, a trial wave function is projected over the best wave function with the same nodes. In DMC the final wave function is unknown but the expectation value of the energy is normally very close to the exact one.

In this work, we use VMC to compute the electronic wave function and, from  $|\Psi_{VMC}|^2$ , the electronic configurations to evaluate the fluctuations of the damped field defined in Eq(10). As we can see from Eq(9), this is not sufficient to get all information for the calculation of vdW coefficients. We have in fact two unknown quantities, namely  $\alpha$  and  $I$ . If we have a method to compute the dipolar polarizability  $\alpha$ , we can use Eq(9) to get  $I$ . To this purpose, following the basic idea of Huiszoon and Briels<sup>21</sup> and Caffarel et al<sup>22</sup>, we used DMC to compute  $\alpha$  by considering the addition of a constant external electric field. By applying a weak external field  $\mathcal{E}_{ext}$  we can write

$$E_{DMC}(\mathcal{E}_{ext}) = E_{DMC}(0) + \frac{1}{2}\alpha\mathcal{E}_{ext}^2 + \dots \quad (\mathcal{E}_{ext} \rightarrow 0) \quad (14)$$

which allowed us to estimate  $\alpha$  by fitting the DMC energy computed at various external field values. Thus, by combining VMC and DMC it is possible to get the information requested to compute the vdW  $C_6$  coefficients for any pair of atoms in ground or excited states.

## The dispersion energy with a ‘model atom’

With the computed  $\alpha$  and  $I$  we can reproduce the dispersion energy between two atoms only at very large distance. However, at smaller distances we can attempt to compute at least a large fraction of the dispersion energy by using the following function

$$S^2(\mathbf{r}) = \frac{1}{4}\sigma_L^2 + \sigma_{T_1}^2 + \sigma_{T_2}^2 \quad (15)$$

which, thanks to the damping factor  $f_2$ , does not diverge. For example, if one of the two interacting atoms responds only through a dipolar polarization, the following approximation

$$E_{AB}^{(disp)} \approx - \frac{S_A^2(\mathbf{R}_B)\alpha_B}{1 + I_A/I_B} \quad (16)$$

behaves exactly as  $-C_6^{(AB)}/R_{AB}^6$  when  $R_{AB} \rightarrow \infty$  and can work properly at short distances with a given choice of the parameter  $b$  defining the damping factor  $f_2$ . Of course, Eq(16) is not symmetrical because the function  $S^2$  includes also higher order multipole contributions, which are negligible at large but not at short distances, while  $\alpha$  describes only dipolar polarization.

We remark that the field given in Eq(10), apart for the damping factor, is the total electronic field when it is averaged over  $|\Psi|^2$  and, therefore, it includes all the contributions arising from a multipolar expansion. Multipolar expansions are typically used to decompose the dispersion energy in a sum of terms of which the London formula is the leading one at very large separation. We expect that Eq(16) should account for a large fraction of the dispersion energy because it can bring contributions beyond the dipole-dipole mutual polarization.

A further important feature of Eq(16) is that the system interacting with the "model atom" can be also a molecule because  $S^2(\mathbf{r})$  can be computed, in general, for any polyatomic system. This generalization will be an objective of a further work. Here, we limit to say that the calculation of  $S^2(\mathbf{r})$  does not require, in principle, any decomposition in atomic contributions, this function being generated by a total electronic field. On the contrary, the 'model atom' can be viewed as an interacting atomic site in a molecule and thus, one further extension of the present approach could lead to the calculation of molecule-molecule dispersion

energy. Similar simpler treatments based on atoms in molecules, and again based on London's formula, are currently used to introduce dispersion interactions in density functional theory (DFT)<sup>23-25</sup>.

## Towards a continuum model for solvation

The approximate expression given in Eq(16) for dispersion energy is suitable for a further elaboration in the context of continuum models for solvation. In this equation, we assume an interaction of a given molecule with a model system identified by an average static dipolar polarizability  $\alpha_B$  and an ionization potential  $I_B$ . If we take a continuum medium generated by a continuous distribution of such model subunits, the dispersion contribution to the free energy of solvation of a given solute, can be written as

$$\Delta G_{disp} \approx - \int d\mathbf{r} \frac{S_A^2(\mathbf{r})\alpha_B\rho_B(\mathbf{r})}{1 + I_A/I_B} \quad (17)$$

in which we assume that the numeral density  $\rho_B$  of the continuum  $B$  (the solvent) does not depend on the charging of the dispersion interaction. Here, the solute is labeled with the letter  $A$  and is characterized by the electronic field fluctuation function  $S_A^2$ . As in the Floris and Tomasi model<sup>9,10</sup>,  $\rho_B$  will be assumed constant and equal to the bulk value in the solvent domain while is assumed to be zero inside the cavity ( $\mathcal{C}_A$ ) where the solute molecule is placed. At this point, we can make use of the Clausius-Mossotti equation

$$\frac{\eta^2 - 1}{\eta^2 + 2} = \frac{4\pi}{3}\rho\alpha \quad (18)$$

which allows us to rewrite Eq(17) in terms of a macroscopic property of the dielectric, namely the refractive index  $\eta_B$  of the solvent. By restricting the integral to the solvent

domain, the dispersion free energy of solvation becomes

$$\Delta G_{disp} \approx - \frac{3(\eta_B^2 - 1)}{4\pi(\eta_B^2 + 2)(1 + I_A/I_B)} \int_{\mathbf{r} \notin \mathcal{C}_A} d\mathbf{r} S_A^2(\mathbf{r}). \quad (19)$$

It is interesting to note that this equation is not anymore restricted to atoms but can be used also for molecular solutes. Of course, in such a case, due to the reduced symmetry,  $S_A^2(\mathbf{r})$  must be computed over a more complex grid to evaluate the integral above. Another interesting feature of Eq(19) is that it can be applied to solutes in an excited electronic state.

## Illustrative examples

In order to demonstrate the reliability of the QMC approach described above to compute  $C_6$  dispersion coefficient, we show the results on He and Ne atoms. Furthermore, we provide as test examples of computing the  $\Delta G_{disp}$  the case of solvation of He, Ne and  $F^-$  in water as solvent.

## Computational details

The QMC calculations were carried out with the program package CHAMP<sup>26</sup>. We employed scalar-relativistic energy-consistent Hartree-Fock pseudopotentials<sup>27</sup> with modified VTZ basis sets (see, Supplementary Information). We prepared the starting determinantal component of the Jastrow-Slater wave function in configuration interaction with single and double excitations (CISD) calculations performed with the program GAMESS(US)<sup>28</sup> for He. We limited to a one determinant for Ne and  $F^-$ . We employed a three-body Jastrow factor to account for electron-nuclear, electron-electron, and electron-electron-nucleus correlations<sup>20</sup>. The QMC wave functions were fully optimized within variational Monte Carlo using the linear method<sup>29</sup> and its extension to state-average calculations<sup>30</sup> for the singlet excited state of He. We used a time step of 0.05 a.u. in the fixed-node DMC calculations in

which the pseudopotentials have been treated beyond the locality approximation<sup>31</sup>.

## The He atom

For He we studied the ground ( $1^1S$ ) and the first singlet ( $2^1S$ ) and triplet ( $2^3S$ ) excited states. We used different basis sets for ground and excited states because of the very different spatial electronic distributions. In Figure 1, we show the fractional number of electrons escaped from a sphere centered on the nucleus as a function of the sphere radius for all the atomic systems considered in this work. This function gives immediately an idea of the tail profile of the atomic electron distribution. We can see from this plot that while for He in the ground state practically all the two electrons (about 99 per cent) are contained inside a sphere of 3 bohr, we need about 10 and 13 bohr for, respectively, the triplet and the singlet excited states in order to have the same confinement. The quantity plotted in Figure 1 was obtained from a set of electronic configurations generated at the VMC level. For this atom, we performed VMC calculations to optimize the wave function obtained from a CISD combination of Slater determinants multiplied by the Jastrow factor at different values of a constant external electric field. Information on the range of the field used in the three cases is provided in the Supplementary Material. The configurations generated for the atom in absence of external field were used to compute the fluctuations of the electronic electric field needed to compute the average ionization potential  $I$  (see, Eq(9)). The optimized VMC wave functions were subsequently employed as trial wave functions for the DMC calculations to get the polarizability  $\alpha$  following Eq(14) (see Supplementary Information for the relevant plots).

In Table 1, we report the polarizability  $\alpha$  for all the cases studied in this work, the average ionization potential  $I$  together with the limit of Eq(9). We can see immediately that there is a big difference between ground and excited state values of  $I$ . While  $I$  is 1.08 hartree for the  $1^1S$  state, it is much smaller, respectively 0.049 and 0.037 hartree, for  $2^3S$  and  $2^1S$  states. Although there are not available data to compare, these results are

consistent with what one expects. In Table 1, we report also the best literature values of  $\alpha$ . For  $1^1S$  and  $2^3S$  states, our values are in agreement within the statistical errors while for  $2^1S$  state the polarizability is underestimated although the discrepancy is within 25 percent of the best value. Nevertheless, considering the purposes of the present work it seems that this is sufficient to compute a reliable value of  $C_6$  as we show in Table 2. In this Table, we report the resulting  $C_6$  dispersion coefficients for all the possible pairs of He atoms in the three studied electronic states. In all cases, we found an agreement with literature data within the statistical error. These discrepancies seem to be large, being about 10 per cent, but the propagated error in the dispersion energy could be acceptable.

Now, it is interesting to analyze the fluctuations of the damped electric field defined in Eq(10) in order to gain information on dispersion energy at short distances. We limit this analysis to the He dimer in the ground state because the atomic volumes of He atom in the excited states are large and also He in these states tends to form strongly bounded excimers<sup>32</sup>. In Table 1 we report the chosen values of the parameter  $b$  entering in the damping function  $f_2(r)$ . These are not optimized but are reliable values related to the atomic radii, which can be determined from the quantity plotted in Figure 1. We have noticed in fact that, after looking at the final dispersion energy plots of pairs of atoms, a working empirical formula for  $b$  in bohr<sup>-1</sup> can be the following

$$b = 1.1 + \frac{1.6}{R} \quad (20)$$

where  $R$  is the radius in bohr of a sphere which leaves outside 0.5 electrons (see Figure 1). In this respect,  $R$  may be viewed as a hard atomic or ionic radius. It is worthwhile to notice that these  $b$  values are very close to the exponential Born-Mayer  $b$  parameters<sup>33</sup>. In Figure 2, we compare the derived interaction dispersion energy computed according to Eq(16) for He dimer with accurate benchmark calculation from literature<sup>34</sup>. With the chosen value of  $b$ , the agreement is good also at distances of 3 bohr at which there is a strong overlap between the two He atoms. It is important to notice that, if our field fluctuations are able

to provide multipolar polarization at short distances, the first term in our model that is lost in this case is a quadrupole-quadrupole term, one of the two atoms being limited only to dipolar polarization.

## The Ne atom

For Ne in the ground state we used, as said before, a Jastrow-Slater form with only a single determinant. The orbitals were optimized at the VMC level removing the spherical symmetry in order to allow polarization along the external electric field axis to compute the polarizability. The static dipolar polarizability resulted in acceptable agreement with the known literature data<sup>35</sup> (see Table 1). By following the same procedure used for He dimer, we computed the  $C_6$  vdW coefficient for the ground state Ne dimer. This is reported in Table 2 where we can see that it is close to the interval covered by literature data<sup>36</sup>. Also for Ne dimer, we attempted the calculation of dispersion energy at short distance. In Figure 3, we compare our calculations with accurate dispersion energy values computed by Bytautas and Ruedenberg<sup>36</sup>. Again, the agreement is fairly good.

## The fluoride anion

$F^-$  is isoelectronic with Ne, thus we used also in this case a single determinant Jastrow-Slater wave function and we followed the same approach shown above for Ne. The computed static dipolar polarizability is in the range of literature data obtained with correlated methods<sup>37</sup>. The average ionization potential  $I$  is smaller than that found for Ne has one can expect.

## Dispersion contribution to the free energy of solvation

We have considered three cases, He, Ne and  $F^-$  in their ground state in aqueous solution. For these three systems we can compare with the recent calculations of Duignan et al<sup>17</sup>. For

an atomic solute, the function  $S^2$  giving the fluctuations of the damped electric field depends only on the distance from the nucleus due to the spherical symmetry. Thus, the integral in Eq(19) can be solved analytically considering a radial function fitting  $S^2$ . We plot the resulting  $\Delta G_{disp}$  in Figure 4 as a function of the cavity radius. In order to reproduce the values of Duignan et al, respectively  $-6.5$ ,  $-12.0$  and  $-100.5$  kJ/mol for He, Ne and  $F^-$ , the cavity radii need to be 4.10 bohr for He, 4.27 bohr for Ne and 3.43 bohr for  $F^-$ . Following Floris and Tomasi<sup>9,10</sup>, the cavity radius for hydrophobic solutes should be defined as a sum of vdW radii of solute and water molecule. In the present study, this should apply to He and Ne but not to  $F^-$ . In fact,  $F^-$  forms H-bonds with water in which we have a relatively strong overlap of  $F^-$  and water electron distributions (see, for example, Amovilli et al<sup>38</sup>). This seems to be consistent with a cavity radius of 3.43 bohr. In general, the problem of defining an appropriate cavity, considering both size and shape for polyatomic molecules, is the same of all PCM based methods and needs a systematic study.

## Conclusions

Starting from London’s interpretation of dispersion forces, we have presented a method, based on QMC in the VMC approach, to measure the electronic electric field fluctuations that can be used to evaluate the strength of such interactions between two atoms or molecules. In the measure of this field fluctuations we have introduced a damping factor in order to remove short-range one-electron terms which would lead to divergences in the variance, namely the measure of the fluctuation, when the two sub-systems overlap. The damping is also effective on the two-electron contributions to the square of the field but it vanishes when the two interacting systems are well separated due to an exponential decay. Such effect is similar to that introduced by the damping factors of Tang and Tonnies<sup>19</sup>. By coupling the measure of the field fluctuation with the calculation of static dipole polarizability, it is possible to compute the dispersion  $C_6$  vdW coefficients for any pair of atoms in ground or excited states through the London formula<sup>1</sup>. This step needs the definition of an average ionization

potential by means of the Unsöld’s approximation<sup>18</sup>, here extended to all bound states of interest. The dipole polarizability can be efficiently computed with DMC considering the response of each individual atom to a constant weak external electric field. We made calculations for the low lying electronic states of He and for the ground state of Ne. The resulting dispersion  $C_6$  vdW coefficients for the considered pairs of interacting atoms were in agreement with literature data within the statistical error of the method.

In this work, we have also attempted the calculation of dispersion energy at short interacting distances exploiting the flexibility in the choice of the exponential decay constant in the field damping factor. With a choice of this constant very close to the Born-Mayer exponential parameter<sup>33</sup>, we have found He–He and Ne–Ne dispersion energy curves in close agreement with existing benchmark calculations. The approach can be generalized to any pair in which one of the two interacting systems is seen as a model atom responding only through a dipolar polarization. This feature has been used to introduce a new approximate expression for the evaluation of the dispersion contribution to the free energy of solvation in a PCM framework by means of the Clausius-Mossotti equation. As in the method of Amovilli and Mennucci<sup>12</sup>, also in this new approach is requested the knowledge of the solvent refractive index and ionization potential while, instead, the solute is treated in a different way at VMC level to get the relevant information from the fluctuations of the electronic electric field. The solute is placed in a cavity of the dielectric as usual. The method has been tested on three spherical solutes, namely He, Ne and  $F^-$  in the ground state and in water as solvent. With a reasonable choice of the cavity radius, the computed dispersion contribution to the free energy of solvation,  $\Delta G_{disp}$ , is in agreement with existing data calculated from different models. This result, namely a new formula to compute  $\Delta G_{disp}$ , is the main achievement of the present study.

The present method of calculation of  $\Delta G_{disp}$  can easily be extended to non spherical solutes also in an excited states and used in the global solute wave function optimization. We think that this step will be very useful in evaluating the solute-solvent dispersion interaction

effect in vertical transition to simulate spectra measured in solution. It is known that standard PCM calculations performed by including only the electrostatic contribution is not able to reproduce, in general, the experimental solvatochromic shift although it includes a large fraction of the solvent effects (see, for example, Floris et al.<sup>39</sup>). In a very recent work, Cupellini et al<sup>40</sup> extended the Amovilli and Mennucci method to the time-dependent density functional theory (TDDFT) and have shown that solute-solvent dispersion interactions give a not negligible contribution to the solvatochromic shift in  $n \rightarrow \pi^*$  and  $\pi \rightarrow \pi^*$  transitions for a variety of solutes in cyclohexane as solvent.

### Supporting Information

Atomic basis sets and plots of DMC electronic energy against the external electric field. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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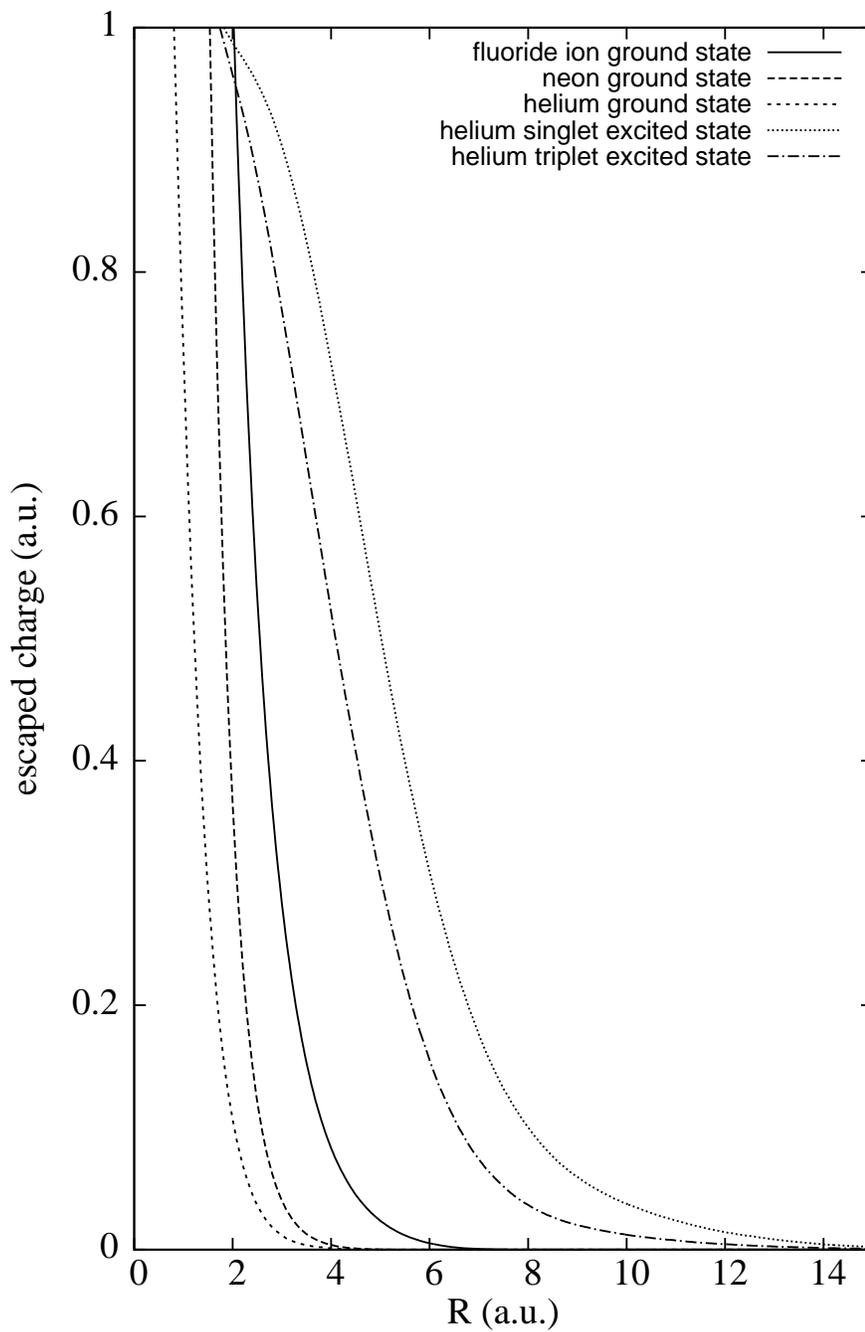


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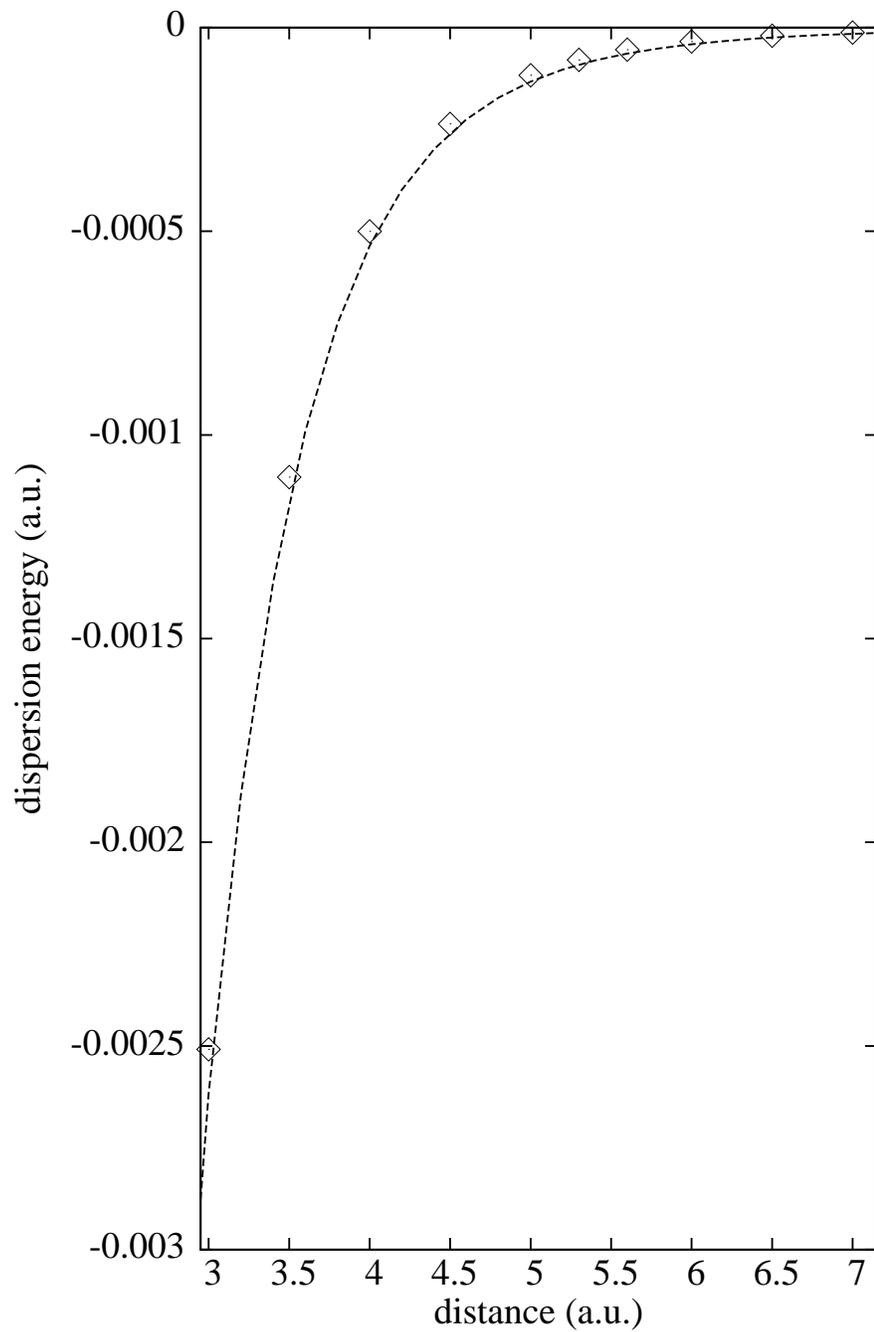


Figure 2: Helium dimer dispersion energy (a.u.) as a function of the distance (a.u.) between the nuclei of the two atoms. Comparison with literature data (diamonds) from Jeziorska et al.<sup>34</sup>.

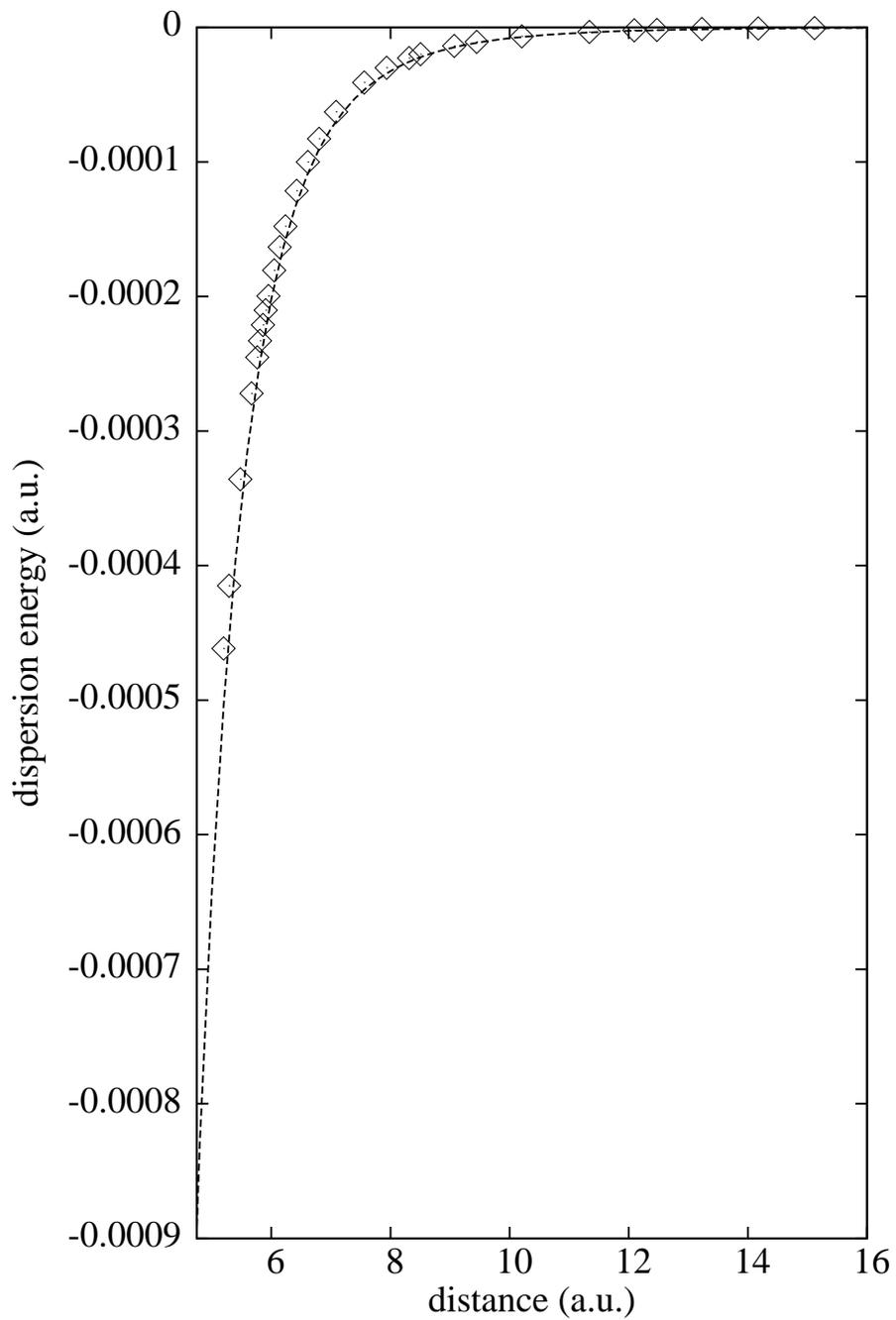


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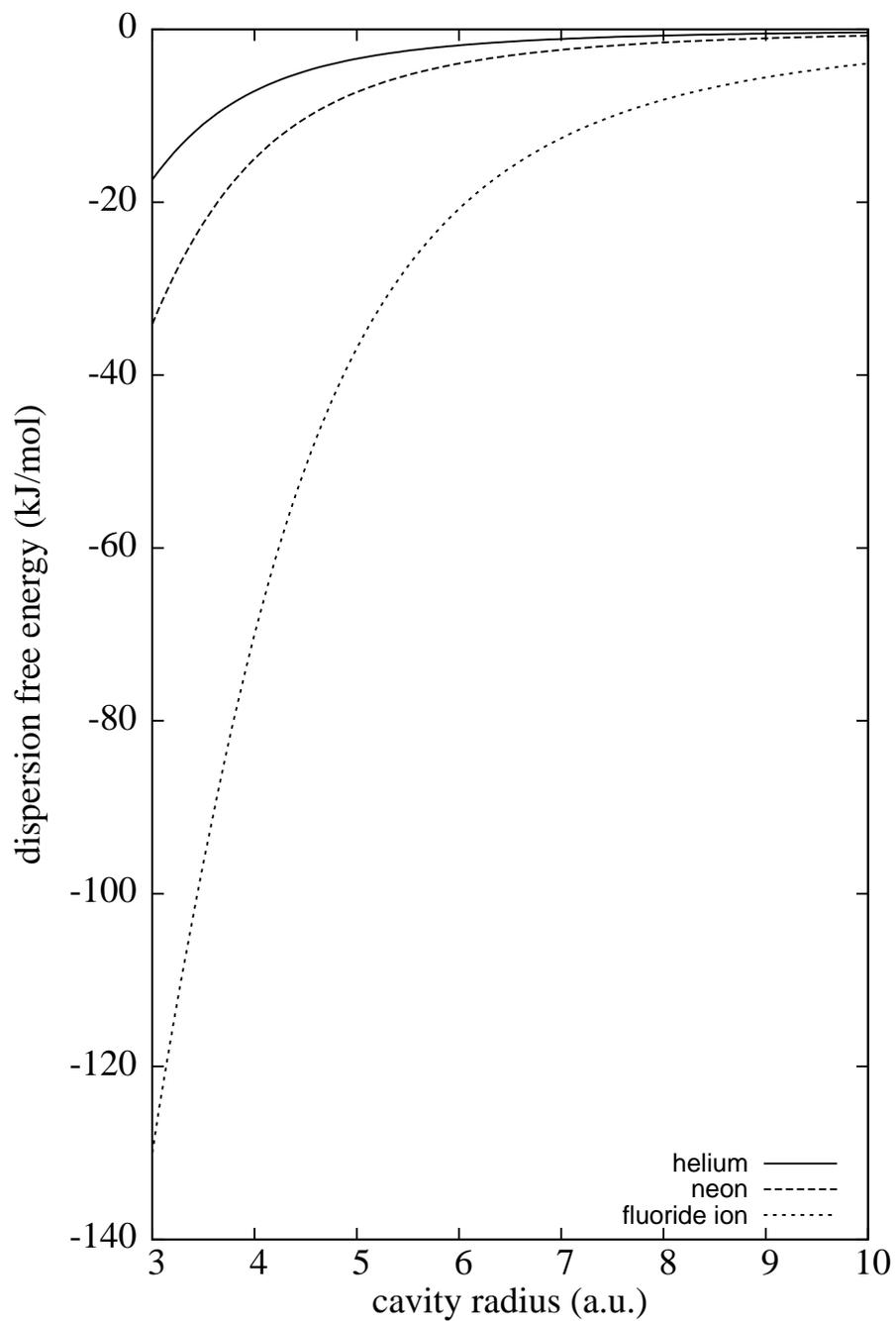


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- 1 QMC results for polarizability  $\alpha$  (bohr<sup>3</sup>) are compared with the best results from the literature ( $\alpha_{lit}$ ) for all the systems and states studied in this work. Quantities derived from the fluctuations of damped electronic electric field (see, Eq(9)), using the damping exponent  $b$  (a.u.) of the table, are also given. 29
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Table 1: QMC results for polarizability  $\alpha$  (bohr<sup>3</sup>) are compared with the best results from the literature ( $\alpha_{lit}$ ) for all the systems and states studied in this work. Quantities derived from the fluctuations of damped electronic electric field (see, Eq(9)), using the damping exponent  $b$  (a.u.) of the table, are also given.

System	State	$\alpha$	$\alpha_{lit}$	$b$	$\lim_{R \rightarrow \infty} S^2 R^6$	$I$
He	$1^1S$	1.39(9)	1.383	2.4	2.25(10)	1.08(10)
He	$2^3S$	313(21)	316.2	1.5	23(1)	0.049(4)
He	$2^1S$	619(11)	800	1.4	34(1)	0.037(2)
Ne	$1^1S$	2.71(1)	2.6695	2.0	5.5(4)	1.35(8)
F <sup>-</sup>	$1^1S$	19(3)	18–20	1.7	10.7(6)	0.37(7)

He data from Ming-Keh<sup>41</sup>

Ne data from Chattopadhyay et al.<sup>35</sup>

F<sup>-</sup> data from Kucharski et al.<sup>37</sup>

**Table 2: Computed  $C_6$  van der Waals coefficients (a.u.) compared with literature data.**

Pair	this work	literature
He( $1^1S$ )–He( $1^1S$ )	1.56(17)	1.461
He( $1^1S$ )–He( $2^3S$ )	30(5)	29.06
He( $1^1S$ )–He( $2^1S$ )	46(5)	41.78
He( $2^3S$ )–He( $2^3S$ )	3600(500)	3268
He( $2^3S$ )–He( $2^1S$ )	6100(600)	5794
He( $2^1S$ )–He( $2^1S$ )	10500(1000)	11180
Ne( $1^1S$ )–Ne( $1^1S$ )	7.45(55)	6.2–7.1

He–He data from Glover and Weinhold<sup>42</sup>

Ne–Ne data from Bytautas and Ruedenberg<sup>36</sup>