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Van der Waals coefficients of atoms and molecules from a simple approximation for the polarizability

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A simple and computationally efficient scheme to calculate approximate imaginary-frequency-dependent polarizability, hence asymptotic van der Waals coefficient, within density-functional theory is proposed. The dynamical dipolar polarizabilities of atoms and molecules are calculated starting from the Thomas-Fermi–von Weizsäcker (TFvW) approximation for the independent electron kinetic energy functional. The van der Waals coefficients for a number of closed-shell ions and a few molecules are hence calculated and compared with available values obtained by fully first-principles calculations. The success in these test cases shows the potential of the proposed TFvW approximate response function in capturing the essence of long-range correlations and may give useful information for constructing a functional which naturally includes van der Waals interactions.

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I. INTRODUCTION

Density-functional theory (DFT) (Ref. 1) has become a standard tool for electronic structure calculations of atoms, molecules, and materials thanks to the widely used local density approximation (LDA) (Ref. 2) and generalized gradient ones (GGA) (Ref. 3) to the exchange-correlation functionals in the Kohn-Sham (KS) formulation. These approximations describe well many properties—such as cohesion, bonds, structures, vibrations, etc.—of densely packed molecules and materials when covalent, metallic or hydrogen bonds are involved. However, they fail when applied to systems having regions of small overlapping density where long-range correlation effects, which are not treated correctly in LDA and GGA, are important. These kinds of systems are frequently met in nature, e.g., in biomolecules, as well as in physical and chemical processes, such as, for instance, in molecular adsorption on surfaces, chemical reactions, etc. The simplest paradigmatic examples of these weakly bonded systems are dimers of noble gas atoms and/or closed-shell molecules and several works in the literature exists where the van der Waals (vdW) C_6 coefficients are calculated within DFT at different levels of sophistication, ranging from a crude treatment of response functions in terms of electronic densities[4] to full calculations within the time-dependent DFT framework.[5]

During the past decade, many attempts have been done to improve performances of DFT calculations in these systems,[6–9] by including explicitly in the exchange and correlation functional nonlocal correlations, that are missing both in LDA and in GGA. The general staring point in all these approaches is the so-called adiabatic connection fluctuation-dissipation (ACFD) (Ref. 10) expression for the exchange-correlation (xc) energy, where an exact formula is used, giving this quantity through dynamical response functions of all fictitious systems which connect the noninteracting KS system with the real many-body interacting one. These calculations are however extremely demanding for practical applications and have been performed only for a limited number of systems so far.[11] Recently, an approximate scheme has been proposed where the ACFD was used as starting point for further simplifications and which has demonstrated to be able to account for van der Waals interaction with some success for a number of cases.[9]

In our opinion, more calculations and further developments need to be pursued in order to explore the potential offered by an approximate treatment of ACFD for the calculation of accurate exchange-correlation energies. Our aim in this work is to assess the possibility of accurately approximating the frequency-dependent response function of a system starting from the Thomas-Fermi and von Weizsäcker (TFvW) approximation for the noninteracting kinetic energy functional. Only the dipolar response function responsible for the asymptotic dispersion interaction between nonoverlapping fragments will be considered here. The encouraging results obtained for the C_6 coefficients will give support to the possibility of using similar procedures in the extremely demanding calculation of accurate correlation energy based on ACFD.

The use of approximate kinetic energy functionals to evaluate dynamical response properties of materials is not a new idea[12] but is a constantly appealing one and, for instance, Barejee and Harbola[13] have recently calculated approximate vdW coefficients for large alkali metal cluster using a TFvW approximation in conjunction with a hydrodynamical approach to the collective excitation of the system.

In this study we follow a different approach to the same problem, where, starting from Thomas-Fermi and von Weizsäcker approximation for kinetic energy functional, we develop a simple and computationally fast procedure to calculate imaginary-frequency-dependent polarizability—hence the van der Waals interaction in the asymptotic region—by density-functional perturbation theory (DFPT).[14–16] Our method contains the following ingredients: (i) the ground-state (GS) electronic density, $n(\mathbf{r})$, which is accurately computed from the standard KS procedure within LDA or GGA;

(ii) a single auxiliary wave function, $\varphi(\mathbf{r})$, corresponding to the GS density, and the auxiliary Hamiltonian admitting $\varphi(\mathbf{r})$ as its GS eigenfunction in the TFvW approximation; (iii) the so-called modified Sternheimer equation which is used to calculate the imaginary-frequency polarizability of the system. This procedure can be considered as a simplification of the one proposed by Mahan[17] and others[18,19] more than 20 years ago for the exact—within LDA/GGA DFT—calculation of atomic and molecular polarizabilities. The original scheme becomes very demanding for systems having a large number of electrons while our approximate treatment, dealing only with one single auxiliary wave function, can deal efficiently with systems of any number of electrons.

This scheme could be a good starting point, we believe, for developing an approximation of the xc-energy functional which is simple enough to allow broad applications but still captures the essence of van der Waals energies.[20] Moreover, it could also be useful for calculating vdW coefficients of fragments which are needed in some semiempirical treatments of vdW energy in DFT such as the damped-dispersion force method.[21,22]

II. THEORY

A. Calculation of van der Waals coefficient within DFPT

From the theoretical point of view, van der Waals coefficients are most conveniently determined through the frequency-dependent polarizability, $\alpha(iu)$, of the system thanks to the relation

$$C_6 = \frac{3}{\pi}\int_0^\infty du\ \alpha_1(iu)\alpha_2(iu). \tag{1}$$

In the framework of density-functional theory, the static polarizability, $\alpha(0)$, can be obtained from the density response of the system under a uniform external electric field (along the z axis) via

$$\alpha(0) = 2\int \frac{z\Delta n(\mathbf{r})}{E}d\mathbf{r}. \tag{2}$$

An efficient computational technique for calculation of density response that avoids the computation of unoccupied states of the independent-particle Hamiltonian has been proposed by Sternheimer[14] more than 50 years ago for atomic polarizability calculations. The method was later modified by Mahan[15] to include a self-consistent treatment of the electrons for the calculation of atomic polarizabilities within density-functional theory in LDA. The linear density response, Δn, to an external perturbation, ΔV_{ext}, is determined by the following self-consistent set of linear equations:

$$\Delta n = 2\sum_i \mathcal{R}e[\psi_i^*\Delta\psi_i], \tag{3}$$

$$\Delta V_{\text{KS}} = \Delta V_{\text{ext}} + \Delta V_H + \Delta v_{\text{xc}}, \tag{4}$$

$$\left[-\frac{\nabla^2}{2} + V_{\text{KS}} - \varepsilon_i\right]\Delta\psi_i = -[\Delta V_{\text{KS}} - \Delta\varepsilon_i]\psi_i, \tag{5}$$

where the sums run on the set of occupied orbitals only.

A generalization of the method for calculation of polarizability at a finite imaginary frequency (see below) was also made by Mahan[17] and was used to calculate the van der Waals coefficients for a number of atomic systems. The method has later been adapted and successfully applied to the case of extended periodic systems where it is better known as density-functional perturbation theory.[16] This approach is exact within LDA DFT, however, computationally demanding since the computational cost grows as the third power of the system size.

B. Calculation of van der Waals coefficient using TFvW functional

One possible way to reduce the computational cost involved in the DFPT calculation of static and dynamical response functions is to approximate the noninteracting kinetic energy with some orbital free functional, as in the TFvW scheme.

Let us assume that the GS density distribution, $n(\mathbf{r})$, of an atomic or molecular system has been computed accurately within the KS scheme, employing, for instance, LDA or GGA as xc functional, and let us introduce the auxiliary wave function $\varphi(\mathbf{r})$, which is normalized to unit and simply related to the electron density as

$$n(\mathbf{r}) = N|\varphi(\mathbf{r})|^2, \tag{6}$$

where N is the number of electrons in the system. The crucial point in our scheme is the assumption that the response of the system around its GS density can be approximated by using the TFvW functional for the kinetic energy. In this approximation the total energy functional in term of $\varphi(\mathbf{r})$ reads

$$E[\varphi] = \alpha\int [N\varphi]^{5/3}d\mathbf{r} + \frac{N}{2}\int |\nabla\varphi|^2 d\mathbf{r} + E_H[\varphi] + E_{\text{xc}}[\varphi] + E_{\text{ext}}[\varphi] - N\mu\left[\int |\varphi|^2 d\mathbf{r} - 1\right], \tag{7}$$

where $\alpha = \frac{3}{10}(3\pi^2)^{2/3}$ and μ is the Lagrange multiplier used to enforce normalization (Rydberg atomic units are used throughout the text). The choice of this approximation is inspired by the fact that the vW correction term gives the exact kinetic energy in regions where only one wave function is relevant, typically the asymptotic region of atoms or molecules. Moreover, the dominant contributions to the polarizability come from the loosely bound electrons in this region that are thus expected to be captured in this approximation.

The corresponding Euler equation of Eq. (7) determines $\varphi(\mathbf{r})$,

$$\left[-\frac{\nabla^2}{2} + V_{\text{ext}} + V_H + v_{\text{xc}} + \frac{k_F^2}{2} - \mu\right]\varphi(\mathbf{r}) = 0, \tag{8}$$

where $k_F(\mathbf{r}) = [3\pi^2 n(\mathbf{r})]^{1/3}$ is the local Fermi wave vector. If $V_{\text{ext}}(\mathbf{r})$ is given, an approximate GS density in TFvW approximation can be obtained by solving this equation. Here we invert the reasoning and the density, hence $\varphi(\mathbf{r})$, is assumed to be given and an auxiliary effective potential, denoted by $V_{\mathrm{eff}}(\mathbf{r})$, is constructed such that the corresponding Hamiltonian admits $\varphi(\mathbf{r})$ as its GS eigenfunction. It can be formally written as

$$V_{\mathrm{eff}}(\mathbf{r}) - \mu = \frac{1}{2}\frac{\nabla^2\varphi(\mathbf{r})}{\varphi(\mathbf{r})}, \tag{9}$$

and $V_{\mathrm{eff}}(\mathbf{r})$ can be found from this equation once $\varphi(\mathbf{r})$ is known, even if some care must be taken in the asymptotic region where the density, and hence $\varphi(\mathbf{r})$, vanishes exponentially.

The linear density response to an external perturbation is determined by the following self-consistent set of equations:

$$\Delta n = 2N\mathcal{R}e[\varphi^*\Delta\varphi], \tag{10}$$

$$\Delta V_{\mathrm{eff}} = \Delta V_{\mathrm{ext}} + \Delta V_H + \Delta v_{\mathrm{xc}} + \frac{k_F^2}{3n}\Delta n, \tag{11}$$

$$\left[-\frac{\nabla^2}{2} + V_{\mathrm{eff}} - \mu\right]\Delta\varphi = -[\Delta V_{\mathrm{eff}} - \Delta\mu]\varphi, \tag{12}$$

where $\Delta\mu = \langle\varphi|\Delta V_{\mathrm{eff}}|\varphi\rangle$, and $\Delta\varphi$, which satisfies the orthogonal condition $\langle\varphi|\Delta\varphi\rangle = 0$, is the first order change of the wave function brought about by the external field. Once this set of equations is solved, static polarizability is calculated from Eq. (2). In order to find the polarizability at finite imaginary frequency, $\alpha(iu)$, the above procedure is slightly modified by adding a frequency term iu to μ, making it become a complex quantity $\mu+iu$.[17] From the imaginary-frequency polarizability, $\alpha(iu)$, the vdW coefficient C_6 can be immediately calculated from Eq. (1).

C. Construction of the effective potential

We have chosen to apply our method to calculate dynamic polarizabilities and vdW coefficients for two kinds of systems, namely, spherically symmetric ions and some simple molecules to demonstrate the efficiency of the method. By exploiting the symmetry properties of the former systems, the GS density $n(\mathbf{r})$ can be calculated very accurately by integrating the radial KS equations on a logarithmic grid with the highly accurate Numerov's algorithm. In this case the effective potential $V_{\mathrm{eff}}(\mathbf{r})$ can be obtained directly from Eq. (9). For the latter, the situation is more complicated because all quantities are calculated within the plane-wave pseudopotential method and are expanded in Fourier components up to a given kinetic-energy cutoff which makes the inversion needed in Eq. (9) numerically difficult. We have overcome this difficulty by an *iterative optimization process* inspired by the method described in Ref. 23, for the determination of the optimized effective potential starting from an accurate density: assuming that at a given iteration, ith, the approximate effective potential is $V^i_{\mathrm{eff}}(\mathbf{r})$ a residual quantity $S^i(\mathbf{r})$ is defined by

$$S^i(\mathbf{r}) = \varphi^*(\mathbf{r})\left[-\frac{\nabla^2}{2} + V^i_{\mathrm{eff}}(\mathbf{r}) - \mu\right]\varphi(\mathbf{r}). \tag{13}$$

This quantity vanishes everywhere only if the Hamiltonian corresponding to this potential admits $\varphi(\mathbf{r})$ as its GS eigenfunction. As long as this is not the case the potential is updated as

$$V^{i+1}_{\mathrm{eff}}(\mathbf{r}) = V^i_{\mathrm{eff}}(\mathbf{r}) + \alpha S^i(\mathbf{r}) + \beta, \tag{14}$$

where α and β are chosen in such a way that the norm of the new residual $\|S^{i+1}\| = \int d\mathbf{r}[S^{i+1}(\mathbf{r})]^2$ is minimized. The process is terminated when the integrated charge difference $\delta n^i = \frac{1}{N}\int d\mathbf{r}|n^i(\mathbf{r}) - n(\mathbf{r})|$ is less than a given threshold, practically chosen to be on the order of 10^{-3}.

III. RESULTS

A. Atomic systems

Numerical results for closed-shell ions show a good agreement with those obtained by Mahan with an accurate but more expensive calculation for a wide range of atomic number and frequency. This can be seen in Fig. 1 where frequency-dependent polarizabilities of some closed-shell ions obtained by the two methods are compared. In Table I calculated values of vdW coefficients for a number of pairs of rare gases are given. Our results are all in the range and at least as accurate as those reported in Ref. 24 when compared to the reference ones.

In Fig. 2 our calculated C_6 values both for homonuclear and mixed pairs of 14 ions are plotted against those reported in Ref. 17. The good agreement between the results obtained by the two methods is indicated by the narrow spread of the points around the diagonal. Quantitatively, the difference never exceeds 25% and in most cases is less than 10%.

B. Importance of using a good charge density

The calculation of van der Waals coefficients presented above is from response functions in TFvW approximation calculated around an accurate charge density. For this purpose, we need to introduce an effective potential admitting the square root of the charge density as its ground-state wave function as already discussed in Sec. II B. One may wonder if this is indeed necessary since it seems natural to calculate the charge density also in TFvW approximation and then use it as input for the calculation of C_6 coefficient. Moreover, doing calculation in this way makes the construction of the effective potential, needed in our calculation, unnecessary because it is determined in the self-consistent solution of Eq. (8). We have tried this option for the case of noble gas atoms and the results are disastrous. For example, C_6 coefficient of He changes from 2.1 a.u. when computed with accurate LDA-DFT charge density to 15.1, and 227.2 (a.u.) when calculated from the charge densities obtained from the solution of the Hartree equation or from solving self-consistently the TFvW approximation. Reducing the weight of the gradient corrected term in the functional to 1/5, an empirical value often used in the literature,[25,26] still gives a very poor result (36.4 a.u.). This behavior is not totally unexpected since it is

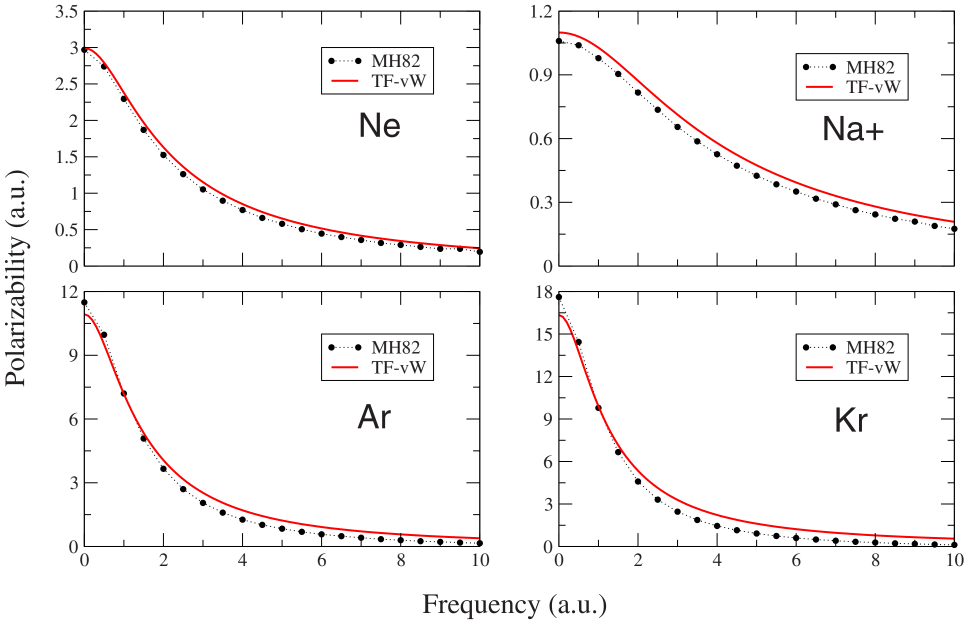

FIG. 1. (Color online) Dynamic polarizabilities of several arbitrarily chosen ions calculated by our method compared to corresponding quantities in Ref. 17.

well known[26] that also the TFvW kinetic energy itself—the quantity on which the approximate response function is based—while giving accurate estimates when applied to accurate charge density behaves poorly if treated self-consistently. This result indicates the importance of calculating the response functions with accurate charge densities and shows that our approach, though not being a self-consistent procedure, is the correct way to calculate vdW coefficient using TFvW approximation.

C. Role of core electrons

For systems without spherical symmetry, the KS equations as well as the modified Sternheimer ones are no longer radial-angular separable, and a general method to calculate GS electronic structures must be used to solve them. The scheme described above has been implemented in the PWSCF plane-wave pseudopotential code which is part of the QUANTUM ESPRESSO distribution.[27] Although in the pseudopotential approach the core-electron density could be easily included in the definition of the auxiliary function, $\varphi(\mathbf{r})$, it is not convenient because of the higher computational cost due to larger kinetic-energy cutoff that would be required in the calculation of the GS density $n(\mathbf{r})$. It is therefore worthwhile to estimate the contribution, expected to be small, of the core electrons to the polarizability in this scheme. To this end, we compared the results obtained in atomic calculations where $\varphi(\mathbf{r})$ was computed from the total charge density or from the valence-only charge density or, as it is done in the nonlinear core correction (nlcc), from the valence charge density plus a smoothed core charge. Here we show the results for beryllium and argon atoms for which the effects of the core charge on the total polarization are expected to be considerably different. It could be not negligible for the former due to non-tightly bound core electrons to a small charge nucleus, while it should be very small for the latter whose core electrons are more tightly bound. It turns out that in both cases the contribution of the core charges to C_6 values is very small. In Fig. 3 static response densities calculated by using different den-

TABLE I. C_6 values for dimers (Ry atomic units). Present: our results. Mahan: calculations from a very similar scheme in Ref. 17. Unified: calculations from Ref. 24 using self-consistent electrodynamics. Reference: values cited as reference in Ref. 24.

Dimer	Present	Mahan	Unified	Reference
He	2.64	3.64	2.58	2.92
Ne	15.44	13.96	15.0	13.8
Ar	133	132.2	143	134
Kr	266	261.4	291	266
Xe	600		663	597

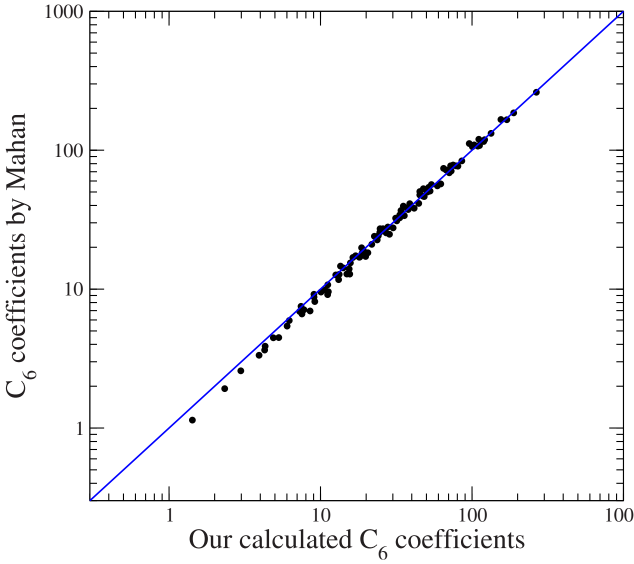

FIG. 2. (Color online) C_6 values of all possible pairs of 14 ions calculated by our method plotted against corresponding values shown in Ref. 17.

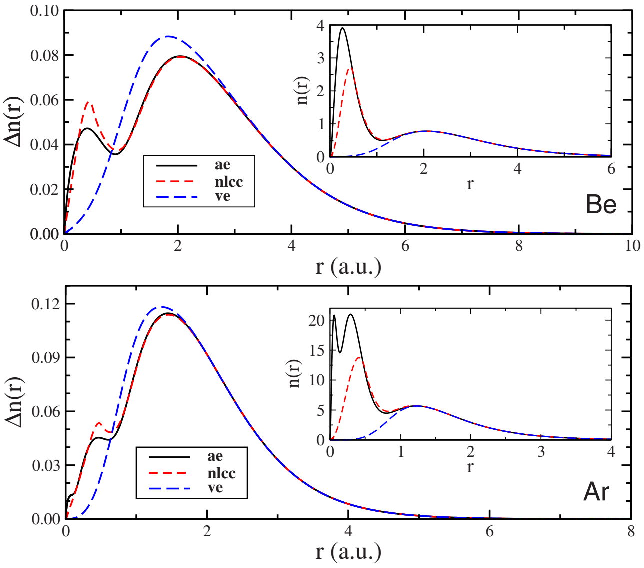

FIG. 3. (Color online) Static density responses of Be (top) and Ar (bottom) calculated with different treatment of the core charge (see the insets): totally included (ae), completely neglected (ve), and partially included (nlcc).

sities in the core region (see the insets) are plotted. This figure shows two opposite roles of core electrons in determining the polarizability. On the one hand, they contribute to the density response in the core region, thus making the total polarizability larger. They prevent, on the other hand, penetration of valence electrons into the core region when an electric field is applied, therefore reducing the total polarizability. Although these contributions do not cancel each other exactly, they still make the effects of the core charge not very important as indicated by the values of static polarizabilities and C_6 coefficients reported in Table II, where the difference between totally included and completely neglected core charge is just a few percent. Therefore, in the calculations for molecules presented below, a little accuracy has been sacrificed by using only the density of valence electrons in order to reduce the number of plane waves needed to describe the auxiliary wave function of the system.

D. Molecular systems

To exemplify the general scheme, we have calculated dynamic polarizabilities and vdW coefficients of methane and benzene, two molecules with different nature of chemical bonds and geometric structures. The KS equations for each isolated molecule were solved using periodic boundary conditions in a simple cubic simulation cell with side length of 12 and 10 Å and kinetic-energy cutoffs of 80 and 60 Ry, respectively. Simple LDA exchange-correlation functional with norm-conserving pseudopotentials was used to obtain the GS charge density of the isolated molecules.

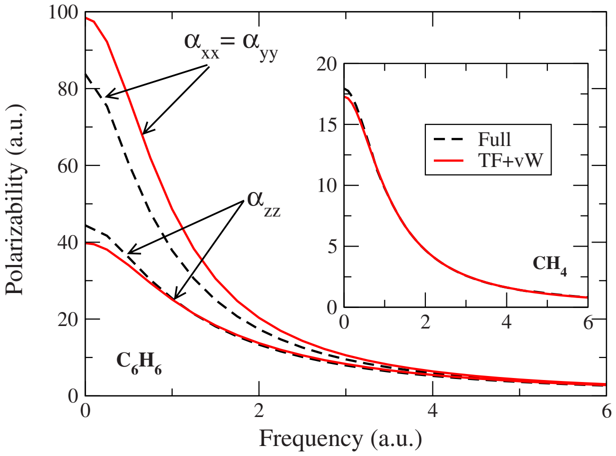

FIG. 4. (Color online) Imaginary-frequency dependent polarizabilities of methane (the inset) and benzene molecules calculated by TFvW method (solid red curves) compared to results of full calculation (dashed black curves).

Figure 4 shows the imaginary-frequency dynamic polarizabilities of methane and benzene molecules calculated in our scheme, compared with the result of the full calculation which has also been implemented in the PWSCF plane-wave pseudopotential code. For methane molecule, the result of our simplified calculation compares excellently with the one of the more accurate methods. Although this is not the case for benzene molecule, nevertheless, the difference between the two calculations is still rather moderate as expected.

From the dynamical polarizability the C_6 coefficients can be obtained and the approximate calculation agrees very well with the full calculation for methane (264 a.u. to be compared with 271 a.u. obtained in the full calculation) while for benzene TFvW approximation overestimates by about 40% the full calculation (4.9×10^3 a.u. with respect to 3.6×10^3 a.u.).

IV. DISCUSSION AND CONCLUSION

In this study we have shown that a simple approximation for the (dynamical) polarizability of atoms and molecules

TABLE II. Static polarizabilities $\alpha(0)$ and vdW coefficients C_6 (Ry atomic units) of Be and Ar calculated with different densities: all-electron (ae), valence with some core-charge (nlcc), and only valence electron (ve) density.

	$\alpha(0)$			C_6		
	ae	nlcc	ve	ae	nlcc	ve
Be	33.07	33.05	33.54	194.10	194.14	190.58
Ar	10.93	10.92	10.96	66.80	66.85	63.80

can be obtained starting from the TFvW approximation to the independent electron kinetic energy functional. The success of the present approximate method in the calculation of frequency-dependent polarizability and vdW coefficients of atomic and molecular systems, together with its computational efficiency, especially for large systems, suggests that it may be a useful tool to explore the behavior of systems where nonlocal long-range correlations are important.

An algorithmic development of time-dependent density-functional theory in real time has recently been proposed by Marques *et al.*[28] that allows for an efficient evaluation of van der Waals coefficients from the full Kohn-Sham response function. The computational cost for the calculation of C_6 coefficients in this approach grows quadratically with the system size. In our approximate scheme instead the computational cost grows only linearly with the size of the system. This is because only one auxiliary wave function is needed no matter how many electrons are present in the system. Even for the small atomic and molecular systems considered in this work the computational time required by the simplified calculation is at least one order of magnitude lower than that of the full calculation and this is expected to become increasingly more convenient for larger systems. Only a systematic comparison of the results obtained for more systems within our approximate scheme as well as within other approaches will allow to better assess the computational and physical merits and limitations of the various approaches.

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