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Long-range van der Waals interactions in density functional theory

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Abstract The early difficulties in accounting for long-range van der Waals interactions in the framework of density functional theory (DFT) have been overcome to a certain extent in recent works by several groups, and those interactions can be computed numerically. In this paper a derivation of the analytical form of the attractive van der Waals interaction between two neutral atoms with polarizabilities α_1 and α_2 at large distance R, namely $E_{\text{int}} = -C_6\alpha_1\alpha_2/R^6$ is performed within the context of DFT. Use is made of the properties of the Coulomb correlation hole, and it is shown that nonlocal Coulomb correlations are responsible for long-range dispersion interactions.

Keywords Atoms · Molecules · van der Waals interaction · Electronic correlation · Exchange–correlation hole · Density functionals

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1 Introduction

Density functional theory (DFT) [1–3] is a very successful tool for the study of atoms, molecules, clusters and solid materials with metallic, covalent and ionic bonding. The exchange–correlation energy functional $E_{\text{xc}}[n]$ and the exchange–correlation potential $V_{xc}(\mathbf{r})$ are key ingredients in practical implementations of the DFT. The exact form of $E_{\text{xc}}[n]$ is not known and an enormous effort has been dedicated to obtain improved approximations to the exchange–correlation functional beyond the local density approximation [4,5]. In fact, the present generalized gradient approximation (GGA) functionals lead to impressive results in the simulation of the materials mentioned above [6–8]. In contrast, the treatment of the weak long-range van der Waals forces in DFT has progressed more slowly. Recent work has produced very promising results [9–13], although an accurate treatment simple enough to be incorporated in the usual DFT codes for materials' simulation is still to be developed. The most recent work reproduces in a satisfactory way the magnitude of van der Waals interactions numerically for a variety of materials [9–11]. That is, those interactions arise after elaborate numerical calculations which give the interaction energy for a set of discrete distances R between the two subsystems. However, an explicit derivation of the analytical form of the van der Waals interaction in the framework of DFT, that is, of the usual attractive term $-C/R^6$, arising from a transparent physical mechanism, has not yet been done to the best of our knowledge. Recently, Becke and Johnson [14] have presented a model in which the instantaneous dipole moment of the exchange hole (also called Fermi hole) around an electron in an atom is used to generate a dispersion interaction between nonoverlapping systems. In this paper we present a derivation of the form of the van der Waals interaction in the framework of DFT which is based on a microscopic mechanism fully based on Coulomb correlations. An electron in atom 1 builds a correlation hole that moves around with the electron. At long distance the potential due to this correlation hole behaves, in lowest order, as that of an electric dipole. Then, this electric dipole induces another dipole on a neighbor atom 2, and the interaction between the two dipoles is responsible for the long-range dispersion interaction between the two atoms.

The asymptotic form of the exchange–correlation potential $V_{\text{xc}}(\mathbf{r})$ in the tail of a free atom turns out to be an important ingredient in the method used for deriving the dispersion interactions between atoms. Although the asymptotic form of $V_{\text{xc}}(\mathbf{r})$ is known [15], this result is obtained here (except for a constant factor in one of the terms) in an alternative way using the properties of the exchange–correlation hole. Then, in a second step, the analytical form of the van der Waals interaction between two neutral atoms with polarizabilities

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α_1 and α_2 at large distance R, $E_{\mathrm{int}} = -C_6\alpha_1\alpha_2/R^6$, is obtained.

2 Asymptotic form of the exchange–correlation potential in a neutral atom

The exchange–correlation potential appearing in the single-particle Kohn–Sham equations of DFT is the functional derivative of the exchange–correlation energy functional $E_{\mathrm{xc}}[n]$

$$V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[n]}{\delta n(\mathbf{r})}. \tag{1}$$

Since the exact functional $E_{\mathrm{xc}}[n]$ is not known, the exact potential $V_{\mathrm{xc}}(\mathbf{r})$ is also unknown. However, the asymptotic form of $V_{\mathrm{xc}}(\mathbf{r})$ for a neutral atom (or a molecule) was derived by Almbladh and von Barth [15]. This asymptotic form is

$$V_{\mathrm{xc}}(\mathbf{r}) = -\frac{1}{r} - \frac{\alpha}{2r^4}, \quad r \to \infty, \tag{2}$$

where α is the polarizability of the single-charged positive ion. Almbladh and von Barth obtained this asymptotic form using the Kohn–Sham equations and the asymptotic behavior of the electron density $n(\mathbf{r})$ of the atom. The knowledge of the asymptotic form of Eq. (2) has been of great help in developing and testing approximations to the exchange–correlation potential [16,17]. The asymptotic form given in Eq. (2) is now obtained (except for a constant factor in the second term) using a different method, based on the explicit use of the exchange–correlation hole surrounding an electron. The interest of the alternative method is based on the fact that it serves to enlighten the properties of the exchange–correlation hole and to stress its importance in other applications; those properties will be exploited in Sect. 3.

The exchange–correlation energy can be written as:

$$E_{\mathrm{xc}}[n] = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')[g_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';[n]) - 1]}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r\,\mathrm{d}^3r', \tag{3}$$

where $g_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';[n])$ is the pair correlation function (integrated over the coupling constant for the Coulomb interaction). It is useful to interpret this energy as the interaction between two charge distributions. The first one, $n(\mathbf{r})$, is the electronic density of the system, and the other

$$n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') = n(\mathbf{r}')[g_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';[n]) - 1], \tag{4}$$

represents the exchange–correlation hole around an electron placed at $\mathbf{r}$ (this reduces to the exchange hole, or Fermi hole, if Coulomb correlation is neglected). The exchange–correlation hole accounts for the instantaneous decrease of the electron density at points $\mathbf{r}'$ due to the presence of an electron at $\mathbf{r}$. Performing the variational derivative of the exchange–correlation energy [18,19] one obtains

$$V_{\mathrm{xc}}(\mathbf{r}) = 2V_{\mathrm{xc1}}(\mathbf{r}) + V_{\mathrm{xc2}}(\mathbf{r}), \tag{5}$$

where

$$V_{\mathrm{xc1}}(\mathbf{r}) = \frac{1}{2}\int \frac{n(\mathbf{r}')[g_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';[n]) - 1]}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r' \tag{6}$$

and

$$V_{\mathrm{xc2}}(\mathbf{r}) = \frac{1}{2}\int\int \frac{n(\mathbf{r}')n(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|}\frac{\delta g_{\mathrm{xc}}(\mathbf{r}',\mathbf{r}'';[n])}{\delta n(\mathbf{r})}\mathrm{d}^3r'\mathrm{d}^3r''. \tag{7}$$

Gritsenko and coworkers [20,21] have analyzed the two terms in Eq.(5) for the case of neutral atoms. The first term, $2V_{\mathrm{xc1}}(\mathbf{r})$, is equal to the potential of the exchange–correlation hole and represents the screening of the full Hartree potential by exchange–correlation effects. It was called the screening potential by these authors. The other term, $V_{\mathrm{xc2}}(\mathbf{r})$, which depends on the functional derivative of $g_{\mathrm{xc}}(\mathbf{r}',\mathbf{r}'';[n])$, was called the screening response potential. $V_{\mathrm{xc2}}(\mathbf{r})$ is short ranged in an atom [22,20] and does not contribute to the asymptotic behavior of $V_{\mathrm{xc}}(\mathbf{r})$. Consequently,

$$V_{\mathrm{xc}}(\mathbf{r}) = 2V_{\mathrm{xc1}}(\mathbf{r}), \quad r \to \infty. \tag{8}$$

The leading term, $-1/r$, in the asymptotic behavior of $V_{\mathrm{xc}}(\mathbf{r})$ is easily obtained [22]. Since r is very large, $\mathbf{r}'$ can be neglected with respect to $\mathbf{r}$ in the denominator in Eq. (6). Then

$$V_{\mathrm{xc}}(\mathbf{r}) = \frac{1}{r}\int n(\mathbf{r}')[g_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';[n]) - 1]\mathrm{d}^3r', \quad r \to \infty. \tag{9}$$

The exchange–correlation hole density fulfills a sum rule requiring the normalization of the hole charge

$$\int n(\mathbf{r}')[g_{\mathrm{xc}}(\mathbf{r},\mathbf{r}';[n]) - 1]\mathrm{d}^3r' = -1, \tag{10}$$

that is, a total charge equivalent to one electron is removed from the neighborhood of an electron located at $\mathbf{r}$, building a hole of charge around that electron. Then, Eq. (9) immediately gives the leading term, $-1/r$, in the asymptotic behavior of $V_{\mathrm{xc}}(\mathbf{r})$, since the deficit of electronic charge acts as a positive charge.

To obtain the next asymptotic term it is convenient to separate exchange and correlation. For this purpose one can return to Eq. (4) and separate the exchange–correlation hole density $n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}')$ as a sum of exchange and correlation contributions

$$\begin{aligned} n_{\mathrm{xc}}(\mathbf{r},\mathbf{r}') &= n_{\mathrm{x}}(\mathbf{r},\mathbf{r}') + n_{\mathrm{c}}(\mathbf{r},\mathbf{r}') \\ &= n(\mathbf{r}')\left[g_{\mathrm{x}}(\mathbf{r},\mathbf{r}';[n]) - 1\right] + n(\mathbf{r}')\left[g_{\mathrm{c}}(\mathbf{r},\mathbf{r}';[n]) - 1\right]. \end{aligned} \tag{11}$$

The correlation contribution to $V_{\mathrm{xc}}(\mathbf{r})$, which is the important ingredient in the present discussion, becomes

$$V_{\mathrm{c}}(\mathbf{r}) = 2V_{\mathrm{c1}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')[g_{\mathrm{c}}(\mathbf{r},\mathbf{r}';[n]) - 1]}{|\mathbf{r}-\mathbf{r}'|}\mathrm{d}^3r', \tag{12}$$

with a similar expression for the exchange contribution. The Coulomb correlation hole density $n_{\mathrm{c}}(\mathbf{r},\mathbf{r}')$ has an interesting structure. Since the pure exchange hole also fulfills the sum rule

$$\int n(\mathbf{r}')[g_{\mathrm{x}}(\mathbf{r},\mathbf{r}';[n]) - 1]\mathrm{d}^3r' = -1, \tag{13}$$

this implies

$$\int n(\mathbf{r}')[g_c(\mathbf{r},\mathbf{r}';[n])-1]\mathrm{d}^3r' = 0. \tag{14}$$

That is, Coulomb correlation does not remove a net charge; it simply modulates the instantaneous electronic distribution around the reference electron. Charge is displaced from the close neighborhood of the electron to a more distant region and thus the correlation hole density $n_c(\mathbf{r},\mathbf{r}')$ has regions of negative values and regions of positive values. Since we are interested in evaluating $V_c(\mathbf{r})$ in the limit $r \to \infty$, we perform a multipolar expansion in Eq. (12) and keep the leading contribution, which is an attractive dipolar term

$$V_c(\mathbf{r}) \approx -\frac{D[\mathbf{r}]}{r^2}, \quad r \to \infty, \tag{15}$$

where $D[\mathbf{r}]$ is the effective dipole moment of the correlation hole charge. That is, an electron in the asymptotic tail of the atom views the charge modulation associated to its correlation hole as an electric dipole. This correlation dipole is localized in the bulk of the atom, with its magnitude depending on $\mathbf{r}$, the position of the reference electron in the tail of the atom, and the notation used in Eq. (15) reflects this fact. One can notice that there is no monopole term in the expansion because the net charge of the correlation hole is zero. This, on the other hand, shows that the leading term in Eq. (2) is due to exchange exclusively.

One may wonder if a term similar to that in Eq. (15) could arise from the exchange hole. However, it is known that for $r \to \infty$ in a finite system $n_x(\mathbf{r},\mathbf{r}') = -n(\mathbf{r}')/N_e$, where N_e is the number of electrons [23]. This means that for an electron in the tail of the atom, its exchange hole lags behind and it is spherically symmetric with respect to the position of the nucleus, so the dipolar and higher multipolar components of the exchange hole charge are exactly zero and only the monopolar term, already discussed, contributes in this $r \to \infty$ limit. Consequently, the dipolar contribution to the asymptotic form of $V_{xc}(\mathbf{r})$ in Eq. (2) is due to Coulomb correlation exclusively.

The next step is an estimation of the magnitude of the dipole moment using arguments similar to those of linear response theory. In linear response, the dipole moment induced in a system by an electric field $\mathcal{E}$ is the product of $\mathcal{E}$ and the polarizability of the system. The correlation effect we are discussing is due to the Coulomb interaction. Then, one can argue that for large r, the magnitude $D[\mathbf{r}]$ of the correlation dipole induced in the bulk of the atom by the presence of a reference electron at $\mathbf{r}$ is proportional to the electric field of the reference electron, that is, proportional to r^{-2}. In addition $D[\mathbf{r}]$ has to be proportional to the polarizability α of the single-charged positive ion, since an electron in the tail of the atom leaves behind a positive ion. Consequently, the leading term in the asymptotic behavior of $V_c(\mathbf{r})$ is

$$V_c(\mathbf{r}) = -\frac{c\alpha}{r^4}, \quad r \to \infty. \tag{16}$$

The constant c can be fixed by comparison with Eq. (2), with the result $c = 1/2$.

In summary, the asymptotic form of the exchange–correlation potential in the tail of a neutral atom can be understood as arising from the properties of the exchange–correlation hole left behind by the electron. The leading term is due to exchange, and reflects the fact that the exchange hole removes an amount of charge equivalent to one electron. The next term reflects the fact that the Coulomb correlation hole does not remove a net charge but only displaces charge from the neighborhood of an electron into a more distant region. That term is due to the dipolar component of the Coulomb correlation hole charge.

3 Long-range dispersion interactions between two atoms

Let us now consider two neutral systems, for instance two noble gas atoms, separated a distance R. The correlation energy functional of the system can be written as:

$$E_c[n] = \frac{1}{2}\int\int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\left[g_c(\mathbf{r},\mathbf{r}';[n])-1\right]\mathrm{d}^3r\mathrm{d}^3r'. \tag{17}$$

The case of interest here is when the two atoms, with electron densities $n_1(\mathbf{r})$ and $n_2(\mathbf{r})$, are at distances such that the overlap of the densities is small and there is no electron density redistribution. In this case Eq. (17) can be written as:

$$E_c[n] = \frac{1}{2}\int\int \frac{(n_1(\mathbf{r})+n_2(\mathbf{r}))(n_1(\mathbf{r}')+n_2(\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|} \times \left[g_c(\mathbf{r},\mathbf{r}';[n])-1\right]\mathrm{d}^3r\mathrm{d}^3r'. \tag{18}$$

This notation makes explicit that the pair correlation function is a nonlocal functional of the total density n. The relevant contribution to the long-range interaction comes from the cross terms in Eq. (18), that is,

$$E_{\text{int}} = \int\int \frac{n_1(\mathbf{r})n_2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\left[g_c(\mathbf{r},\mathbf{r}';[n])-1\right]\mathrm{d}^3r\mathrm{d}^3r'. \tag{19}$$

In the limit of negligible overlap between the electron densities of the two atoms

$$E_{\text{int}} = \int_{\Omega_1}\mathrm{d}^3r_1 n_1(\mathbf{r}_1)\int_{\Omega_2}\frac{n_2(\mathbf{r}_2)\,[g_c(\mathbf{r}_1,\mathbf{r}_2;[n])-1]}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}^3r_2, \tag{20}$$

where the notation emphasizes that the integral over $\mathbf{r}_1$ is extended to the volume of atom 1 and the integral over $\mathbf{r}_2$ is extended to the volume of atom 2. The integral over the variable $\mathbf{r}_2$ can be considered as the potential at $\mathbf{r}_1$ due to the correlation charge distribution $n_c(\mathbf{r}_1,\mathbf{r}_2)$ for $\mathbf{r}_2$ restricted to the volume of atom 2, that is,

$$V_c(\mathbf{r}_1) = \int_{\Omega_2}\frac{n_2(\mathbf{r}_2)[g_c(\mathbf{r}_1,\mathbf{r}_2;[n])-1]}{|\mathbf{r}_1-\mathbf{r}_2|}\mathrm{d}^3r_2. \tag{21}$$

In other words, for a reference electron placed at $\mathbf{r}_1$, $V_c(\mathbf{r}_1)$ of Eq. (21) is the potential due to the part of its correlation hole localized in atom 2. This is a fully nonlocal effect of Coulomb correlation: even if the electron densities of atoms 1 and 2 do not overlap, when one electron is on the tail of atom 1, part of its correlation hole is localized in atom 2 because the Coulomb interaction is long ranged. The exact shape of the part of the correlation hole in atom 2 is complex but its qualitative form is simple. Let us consider that the position $\mathbf{r}_1$ of the reference electron is on the tail of atom 1 facing atom 2. The Coulomb repulsion then leads to an instantaneous modulation of the electron density of atom 2: there is a decrease of the probability of finding a second electron on the tail of atom 2 facing atom 1 and a corresponding increase of probability in the inner region of atom 2. Consequently, the reference electron on the tail of atom 1 views the charge modulation associated to its correlation hole in atom 2 as an electric dipole. Again, this intuitive picture can be given a firm mathematical formulation by performing a multipolar expansion in Eq. (21). Since the electron densities of atoms 1 and 2 do not overlap, the sum rule for the correlation hole is also fulfilled for the part of the correlation hole localized in atom 2,

$$\int_{\Omega_2} n_2(\mathbf{r}_2)[g_c(\mathbf{r}_1,\mathbf{r}_2;[n]) - 1]\mathrm{d}^3 r_2 = 0, \tag{22}$$

and the leading term in the expansion is the dipolar term

$$V_c(\mathbf{r}_1) \approx -\frac{D_2[\mathbf{r}_1]}{\mathrm{d}^2[\mathbf{r}_1]} \tag{23}$$

where D_2 is the dipole moment of the part of the correlation hole on atom 2 and d is the distance between the reference electron and the effective location of the dipole. Strictly speaking, the magnitude of the dipole moment depends on the location $\mathbf{r}_1$ of the reference electron, so both D_2 and d are implicit functions of $\mathbf{r}_1$ and the notation used in Eq. (23) reflects this fact. The interaction energy between the two atoms then becomes

$$E_{\mathrm{int}} = \int_{\Omega_1} n_1(\mathbf{r}_1)V_c(\mathbf{r}_1)\mathrm{d}^3 r_1 \approx -\int_{\Omega_1} n_1(\mathbf{r}_1)\frac{D_2[\mathbf{r}_1]}{\mathrm{d}^2[\mathbf{r}_1]}\mathrm{d}^3 r_1. \tag{24}$$

Assuming a weak dependence of D_2 on $\mathbf{r}_1$ and noticing that d can be approximated by the distance R between the two atoms lead to $V_c(\mathbf{r}_1) \approx -D_2/R^2$. Now using the same argument as in Sect. 2 to estimate D_2 , the leading term in the asymptotic behavior of $V_c(\mathbf{r}_1)$ becomes

$$V_c(\mathbf{r}_1) \approx -\frac{\alpha_2}{2R^4} \tag{25}$$

where α_2 is the polarizability of the neutral atom 2. There is no difficulty with the fact that the reference electron is in atom 1 and the correlation dipole in atom 2, because we are dealing with Coulomb interactions; this can be viewed as a nonlocal effect of Coulomb correlation. Returning to Eq. (24), the direct interaction energy between the two atoms can be written as:

$$E_{\mathrm{int}}(R) \approx -\int_{\Omega_1} n_1(\mathbf{r}_1)\frac{\alpha_2}{2R^4}\mathrm{d}^3 r_1. \tag{26}$$

This result is valid for large R, although not for $R \to \infty$. To appreciate this, let us return to Eq. (24). Here the factor $V_c(\mathbf{r}_1)$, varying as R^{-4}, has to be multiplied by the electron density of atom 1, an exponentially decaying function. So, in practice, the direct interaction decays much faster than R^{-4}.

The similarity between the result in Eq. (25) and the asymptotic correlation potential of an isolated atom studied in Sect. 2 may be noticed. This is not surprising because the two potentials have the same physical origin: the leading (dipolar) component of the Coulomb correlation hole associated to an electron. However, a difference is also evident. The polarizability that appears in the case of an isolated atom is that of the single-charged cation left behind by the electron. On the other hand, for the case of two interacting atoms the polarizability is α_2, that of neutral atom 2 , because the potential arises from the correlation hole that an electron of atom 1 builds in atom 2.

By restricting attention, for the moment, to distances R where Eq. (26) is valid, the factor $\alpha_2/2R^4$ can be moved outside the integral, to obtain

$$E_{\mathrm{int}}(R) \approx -Q_1\frac{\alpha_2}{2R^4}, \tag{27}$$

where Q_1 is the integrated electronic charge of atom 1. However, this overestimates the interaction and a reduced charge, about $Q_1/2$ or even less, is more appropriate. The reason is that sizable contributions to the integral of Eq. (26) only occur when $\mathbf{r}_1$ is on the tail of atom 1 facing atom 2. On the other hand if $\mathbf{r}_1$ is in the region of atom 1 opposite to atom 2, the Coulomb interaction between an electron at $\mathbf{r}_1$ and the electrons of atom 2 will be effectively screened by the electrons of atom 1; in such a case the fraction of the correlation hole $n_c(\mathbf{r}_1,\mathbf{r}_2)$ located on atom 2 is negligible. This effect can be taken into account in an approximate way by extending the integral in Eq. (26) to one half of the volume of atom 1 only, with the result

$$E_{\mathrm{int}}(R) \approx -\frac{Q_1}{2}\frac{\alpha_2}{2R^4}. \tag{28}$$

If the two atoms are different, by repeating the derivation of this equation interchanging the role of the two atoms one obtains $E_{\mathrm{int}}(R) \approx -(Q_2/2)(\alpha_1/2R^4)$. The equality of E_{int} then implies

$$\frac{\alpha_1}{Q_1} = \frac{\alpha_2}{Q_2}, \tag{29}$$

that is, the ratio between the electric dipole polarizability of one atom and its electronic charge should be approximately constant. Due to the approximations made in deriving this relation, one should not expect this result to have general validity. In particular the reduction of Q depends strongly on the valence of the atom, and this is discussed below. The validity of the relation improves by restricting its application to a family of similar atoms down a row of the Periodic Table. Figure 1 shows that the relation works well for the noble gases He, Ne, Ar, Kr, Xe and for the halogen atoms F, Cl, Br, I (the experimental polarizabilities are taken from Refs. [24, 25]); however, as expected, the proportionality constant between α and Q is different in the two groups. Other atomic groups display a similar behavior, with the slope progressively increasing as one moves to the left of the Periodic Table.

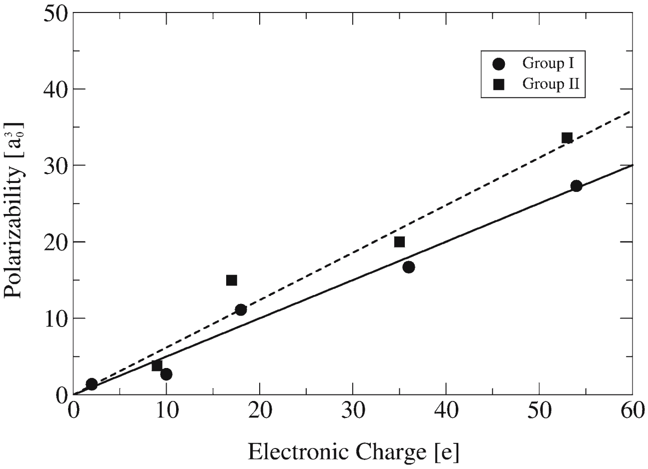

Fig. 1 Measured polarizability versus total electronic charge for noble gas atoms (Group I) and halogen atoms (Group II)

Elements from different groups of the Periodic Table can be related if we notice again that, in practice, only the outermost part of atom 1 contributes to the integral in Eq. (26), because only in such a case there is a part of the correlation hole on atom 2. This can be simulated by considering that a better representation of Eq. (28) is

$$E_{\text{int}}(R) \approx -\frac{Q_1}{2F}\frac{\alpha_2}{2R^4}, \tag{30}$$

where the reduction factor F, higher than 1, is different for different groups of the Periodic Table. This factor takes into account how fast the atomic electron density decays. That decay is controlled by the value of the ionization potential I according to the relation $\rho(r \to \infty) \propto e^{-\sqrt{I}r}$, and I becomes higher as the number of electrons in the outer shell increases [26, 27]. So, the reduction factor F for the inert gases is much larger than for the alkaline atoms. The alternative to Eq. (29) in this case is

$$\frac{\alpha_1 F_1}{Q_1} = \frac{\alpha_2 F_2}{Q_2}, \tag{31}$$

that is,

$$\alpha = b\frac{Q}{F} \tag{32}$$

where the constant b is now universal. Evidently, a reduction factor F that increases by moving from the left to the right of the Periodic Table accounts for the reduction of slope observed in Fig. 1 when the number of electrons in the outer shell increases. In summary, the result in Eq. (26) or (30) can be interpreted as giving the leading term in the interaction between the two atoms for R large but not for $R \to \infty$.

To obtain the van der Waals interaction between atoms 1 and 2 we start again by considering that an electron in atom 1 is surrounded by its Coulomb correlation hole, so when this electron moves around, its correlation hole moves with it. We have studied in Sect. 2 the limiting case when this reference electron is in the tail of the atom, but now we are not restricted to that limit; that is, we are also interested in positions $\mathbf{r}_1$ of the electron in the bulk of atom 1. The potential that the correlation hole of this electron creates at a distant point $\mathbf{R}$ can be expanded in multipolar components. The lowest order term in the expansion is the dipolar term, $-D_1 R^{-2}$, where D_1 is the dipole moment of the correlation hole density $n_c(\mathbf{r_1}, \mathbf{r}')$. The calculation of the correlation hole density is very difficult. For this purpose a precise description of Coulomb correlation, beyond the level presently available in the usual implementations of DFT, would be required. This makes difficult even a rough estimation of the dipole moment D_1, but since the correlation hole consists in an instantaneous internal rearrangement of the distribution of the electrons of atom 1 around a reference electron, the magnitude of D_1 should be proportional to the polarizability α_1 of the atom. The electric field of this dipole is of the form $\mathcal{E} = D_1 R^{-3}$. This electric field induces a correlation dipole in atom 2

$$D_2^{\text{ind}} = \alpha_2 \mathcal{E}, \tag{33}$$

where α_2 is the polarizability of that atom, and the attractive interaction between the fluctuating dipole in atom 1 and the induced dipole in atom 2 is

$$E_{\text{int}}^{\text{dd}}(R) = -\frac{D_1 D_2^{\text{ind}}}{R^3}. \tag{34}$$

Finally using the above results for D_1 and for the induced dipole moment D_2^{ind} gives the van der Waals interaction energy

$$E_{\text{int}}^{\text{dd}}(R) = -C_6 \frac{\alpha_1 \alpha_2}{R^6}, \tag{35}$$

where all the proportionality factors have been included in the constant C_6. We point out that the method employed to derive van der Waals interactions is similar to that used by Becke and Johnson [14], but a key physical ingredient is different: we use the Coulomb correlation hole as the ultimate origin of these forces, instead of the exchange hole. The two contributions represented by Eqs. (26) and (35) can be considered as the two first terms in an expansion of the interaction energy of Eq. (19).

4 Discussion and summary

Evidently, at its present stage of development the method presented in this paper does not allow for the application of DFT to calculate van der Waals interactions between two atoms or two molecules quantitatively because this is an asymptotic result; that is, as the distance R between the two atoms decreases and the overlap between the electron densities n_1 and n_2 increases, some of the approximations used here would have to be improved, and the precise form of the correlation hole needs to be modeled in detail. However, the intention of this work is not to provide a practical scheme to quantitatively calculate van der Waals interactions. Instead, the purpose is to illustrate how the van der Waals forces arise in a DFT framework, and to identify the microscopic mechanism in terms of concepts used in DFT. In fact, the work shows that these long-range interactions are due to fully nonlocal Coulomb correlation effects between the electrons in different atoms, and in particular to the leading (dipolar) component of the correlation hole when two atoms are sufficiently far apart. This picture, not recognized until now, is at variance with a recent model in which the instantaneous dipole moment of the exchange hole in an atom is used to generate a dispersion interaction between nonoverlapping systems [14].

In addition, the derivation provided here makes clear that the term R^{-6} dominates only at sufficiently large R, when other shorter-range interactions have already vanished. This is, in our opinion, the reason for the unexpected reasonable performance of simple density functionals in some cases involving weak interactions, for instance the physisorption of molecular hydrogen on the surface of graphite and carbon nanotubes [28–31], or the physisorption of benzene on the surface of carbon nanotubes [32]. In other words, we think that the weak binding in those cases is due, in a substantial part, to the nonnegligible overlap between the electron density tails at the equilibrium separation and to the small redistribution of the electron density. The van der Waals interaction becomes effective only at higher separations.

In summary, the asymptotic form of the exchange –correlation potential of DFT in the tail of a neutral atom, given in Eq. (2), has been derived (except for a constant factor in the second term) using a method relying on the properties of the exchange–correlation hole. In a second step, the analytical form of the long-range van der Waals interaction between two atoms has been obtained. These forces can be viewed as arising from a mechanism fully controlled by Coulomb correlations. An electron of atom 1 builds a correlation hole around it that moves with the electron. Far from the atom, the electric field due to this correlation hole behaves in leading order as a dipolar field. This correlation dipole induces another correlation dipole in atom 2, and the interaction between the two dipoles leads to the long-range dispersion interaction. The work makes clear that this is an asymptotic result, valid when the distance between the two atoms is large enough.

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