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Van der Waals interaction between atoms: Finite-size effects

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An analysis is made of the theory of Van der Waals interaction between atoms by means of linear-response theory. It is shown that the spread of the atomic wave functions leads to removal of divergences at close distances in the interaction in a natural way, while asymptotic large-distance behavior remains unchanged, being of the London form.

I. INTRODUCTION

The dispersion or Van der Waals interaction energy of two atoms or molecules is usually studied in the asymptotic limit in which the distance of separation of the atoms far exceeds the spread of their charge distribution. For smaller distances of separation their finite size would have a role in this interaction. This aspect of the problem has been analyzed phenomenologically by Mahanty and Ninham,[1] and more rigorously by Richardson.[2] The main conclusion of the analysis is that the finite size of the interacting atoms would make the Van der Waals interaction tend to a finite limit at close distances—this applies not only to the London dipole-dipole interaction, but to multipole interactions as well. The object of this paper is to give a unified treatment of Van der Waals interaction between two atomic systems taking into consideration their finite size and thereby automatically including multipolar interactions to all orders.

The method of analysis adopted here is the zero-point energy approach,[1,3] in which the interaction energy of the two atomic systems is expressed as the change in the zero-point energy of the electromagnetic field due to the presence of the systems. This approach is more convenient for our purpose[2] than using time-independent perturbation theory as is usual in the theory of Van der Waals forces.[4] Detailed numerical estimates of the dispersion interaction energy for a real system are not attempted here; but in Sec. IV the main features of the finite size effects will be brought out considering a simple example.

II. THEORY

For completeness, we shall summarize the main points of the zero-point energy method which is well known in literature.[1,3] We shall deal with only those systems in which the magnetic part of the dispersion interaction[5] can be ignored, and shall confine ourselves to the nonretarded situation taking the electrostatic potential as the main form of the interaction. The generalization to include retardation effects, although straightforward, will not be attempted here.

Consider an external potential $\phi_{\text{ex}}(\vec{r}, \omega)$ at frequency ω interacting with two atoms centered at $\vec{R}_{(1)}$ and $\vec{R}_{(2)}$. The atomic system will then be perturbed by an interaction Hamiltonian

$$\mathcal{H}'(t) \equiv H' e^{-i\omega t} = (-e)\left(\sum_j \phi_{\text{ex}}(\vec{R}_{(1)} + \vec{r}_{(1)j}) + \sum_{j'} \phi_{\text{ex}}(\vec{R}_{(2)} + \vec{r}_{(2)j'})\right) e^{-i\omega t} \tag{2.1}$$

where $\vec{r}_{(1)j}$ is the coordinate of the jth electron in atom (1) measured from $\vec{R}_{(1)}$, and likewise for $\vec{r}_{(2)j'}$. The potential energy of each atomic nucleus due to ϕ_{ex} is dropped, since it does not play any role in the analysis.

The change in any property A due to this perturbation can be evaluated by using Kubo's linear-response theory[6] in the form

$$\Delta A_n = \sum_m \left(\frac{\langle n|A|m\rangle\langle m|H'|n\rangle}{E_n - E_m + \hbar\omega} + \frac{\langle n|H'|m\rangle\langle m|A|n\rangle}{E_n - E_m - \hbar\omega} \right) , \tag{2.2}$$

where $|n\rangle$ is the unperturbed state of the system in which we wish to study A, and $\{|m\rangle\}$ is the set of all the unperturbed states, E_m being the energy of the system in the state $|m\rangle$.

Setting in (2.2)

$$A \equiv (-e)\left(\sum_j \frac{1}{|\vec{r} - \vec{R}_{(1)} - \vec{r}_{(1)j}|} + \sum_{j'} \frac{1}{|\vec{r} - \vec{R}_{(2)} - \vec{r}_{(2)j}|} \right), \tag{2.3}$$

we get the potential at $\vec{r}$ induced by the external potential through the atoms at $\vec{R}_{(l)}$, $l = 1, 2$. The secular equation from which the change in the spectral density of the field is obtained, is given by the condition of self-consistency identifying the external potential with the induced potential. We then obtain the secular equation in the form

$$\Phi(\vec{r}, \omega) = \sum_m \left(\frac{\langle n|A|m\rangle\langle m|H'|n\rangle}{E_n - E_m + \hbar\omega} + \frac{\langle m|A|n\rangle\langle n|H'|m\rangle}{E_n - E_m - \hbar\omega} \right), \tag{2.4}$$

where A is given by (2.3)

In terms of Fourier components, (2.4) can be written as an integral equation in $\vec{k}$ space

$$\phi(\vec{k}, \omega) = \sum_{\vec{k}} D(\vec{k}, \vec{k}'; \omega)\phi(\vec{k}', \omega), \tag{2.5}$$

where the explicit form of the kernel $D(\vec{k}, \vec{k}'; \omega)$ is obtained in the following form after some algebra:

$$D(\vec{k}, \vec{k}'; \omega) = \sum_{l, l' = 1}^{2} D_{ll'}(\vec{k}, \vec{k}'; \omega), \tag{2.6}$$

$$D_{ll'}(\vec{k}, \vec{k}'; \omega) = \frac{4\pi e^2}{V} \sum_m \left(\frac{1}{k^2}\right) \times \left(\frac{[f_{mn}^{(l)}(\vec{k})]^*[f_{mn}^{(l')}(\vec{k}')]}{E_n - E_m + \hbar\omega} + \frac{[f_{nm}^{(l)}(\vec{k})]^*[f_{nm}^{(l')}(\vec{k}')]}{E_n - E_m - \hbar\omega} \right) \times e^{-i\vec{k}\cdot\vec{R}_{(l)} + i\vec{k}'\cdot\vec{R}_{(l')}}, \tag{2.7}$$

$$f_{mn}^{(l)}(\vec{k}) = \langle m| \sum_j e^{i\vec{k}\cdot\vec{r}_{(l)j}} |n\rangle, \tag{2.8}$$

and V is the normalization volume of the plane waves used in the Fourier transformation.

The solvability condition for ϕ in (2.5) is the vanishing of the secular determinant

$$|\hat{I} - \hat{D}(\omega)| \equiv |\delta_{\vec{k}\vec{k}'} - D(\vec{k}, \vec{k}'; \omega)| = 0. \tag{2.9}$$

The dispersion energy E_s is obtained from (2.9) using the following formula,[1]:

$$E_s = -\frac{\hbar}{4\pi i} \oint d\omega \ln|\hat{I} - \hat{D}(\omega)| = \frac{\hbar}{4\pi i} \sum_{p=1}^{\infty} \frac{1}{p} \oint d\omega \, \mathrm{Tr}[\hat{D}(\omega)]^p . \tag{2.10}$$

To obtain the dispersion or Van der Waals interaction energy between the two atoms we have to subtract from E_s the dispersion energies of the individual atoms, i.e., of the two-atom system at infinite separation. Up to terms of the order of (e^4) this interaction energy as a function of $\vec{R} \equiv \vec{R}_{(1)} - \vec{R}_{(2)}$ is

$$\begin{aligned} V(R) = {} & \frac{\hbar}{4\pi i} \oint d\omega \Bigg(\sum_{\vec{k}} [D(\vec{k}, \vec{k}; \omega) - D_{11}(\vec{k}, \vec{k}; \omega) - D_{22}(\vec{k}, \vec{k}; \omega)] \\ & + \frac{1}{2} \sum_{\vec{k}, \vec{k}'} [D(\vec{k}, \vec{k}'; \omega)D(\vec{k}'\vec{k}; \omega) - D_{11}(\vec{k}, \vec{k}'; \omega)D_{11}(\vec{k}'\vec{k}; \omega) - D_{22}(\vec{k}, \vec{k}'; \omega)D_{22}(\vec{k}', \vec{k}; \omega)] + \cdots \Bigg) \\ = {} & \frac{\hbar}{4\pi i} \oint d\omega \Bigg(\sum_{\vec{k}} [D_{12}(\vec{k}, \vec{k}; \omega) + D_{21}(\vec{k}, \vec{k}; \omega)] \\ & + \frac{1}{2} \sum_{\vec{k}, \vec{k}'} \{D_{11}(\vec{k}, \vec{k}'; \omega)D_{22}(\vec{k}', \vec{k}; \omega) + D_{22}(\vec{k}, \vec{k}'; \omega)D_{11}(\vec{k}', \vec{k}; \omega) \\ & + F(\vec{k}, \vec{k}'; \omega)F(\vec{k}', \vec{k}; \omega) + F(\vec{k}, \vec{k}'; \omega)[D_{11}(\vec{k}', \vec{k}; \omega) + D_{22}(\vec{k}', \vec{k}; \omega)] \\ & + [D_{11}(\vec{k}, \vec{k}'; \omega) + D_{22}(\vec{k}, \vec{k}'; \omega)]F(\vec{k}', \vec{k}; \omega)\} + \cdots \Bigg). \end{aligned} \tag{2.11}$$

Here, we have

$$F(\vec{k}, \vec{k}'; \omega) \equiv D_{12}(\vec{k}, \vec{k}'; \omega) + D_{21}(\vec{k}, \vec{k}'; \omega). \tag{2.12}$$

Equations (2.11), (2.12), (2.7), and (2.8) constitute the framework of the approach of this paper.

III. FINITE SIZE EFFECTS

Expression (2.11) gives the complete expression for the dispersion interaction energy within the limitation of a linear response theory. If the unperturbed states $|m\rangle$ are chosen as products of the two atomic wave functions, as is usual in the analysis of Van der Waals interactions, it is easy to see that $D_{ll'}(\vec{k},\vec{k};\omega)$ for $l\neq l'$ and hence $F(\vec{k},\vec{k}';\omega)$ will identically vanish. In this case (2.11) becomes

$$V(R)=\frac{\hbar}{4\pi i}\oint d\omega\left(\frac{4\pi e}{V}\right)^2\sum_{\vec{k},\vec{k}',m,m'}\left[\left(\frac{1}{k^2k'^2}\right)\left(\frac{[f^{(1)}_{mn}(\vec{k})]^*[f^{(1)}_{mn}(\vec{k}')]}{E_n-E_m+\hbar\omega}+\frac{[f^{(1)}_{nm}(\vec{k})]^*[f^{(1)}_{nm}(\vec{k}')]}{E_n-E_m-\hbar\omega}\right)\right.$$
$$\left.\times\left(\frac{[f^{(2)}_{m'n}(\vec{k}')]^*[f^{(2)}_{m'n}(\vec{k})]}{E_n-E_{m'}+\hbar\omega}+\frac{[f^{(2)}_{nm'}(\vec{k})]^*[f^{(2)}_{nm'}(\vec{k})]}{E_n-E_{m'}-\hbar\omega}\right)e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}}\right]. \tag{3.1}$$

Two features emerge from this. Firstly, for large R we need the small $(\vec{k},\vec{k}')$ form of the summand above; but from (2.8) it is clear that for $m\neq n$, $f^{(l)}_{mn}(\vec{k})\to 0$ as $k\to 0$, [The term $m=n$ drops out identically in (2.7).] The leading term for $f^{(l)}_{mn}(\vec{k})$ is linear in k, when $|m\rangle$ has opposite parity to $|n\rangle$. It is easy to then show from (3.1) that the $(\vec{k},\vec{k}')$ summation will give us as the leading term $1/R^6$. This is done by replacing the summation by integration. It is also possible to demonstrate that if the exponential function in $f^{(l)}_{nm}(\vec{k})$ is expanded in powers of k, we will get explicitly the various multipolar contributions to the Van der Waals interaction between the two atoms. Thus, (3.1) contains the total Van der Waals interaction when the states $|m\rangle$ are chosen as product wave functions.

Secondly, for $R\to 0$ the summations of $\vec{k}$ and $\vec{k}'$ give finite values in (3.1). This convergence arises from the fact that $f^{(l)}_{mn}(\vec{k})$ will go to zero sufficiently rapidly for large $\vec{k}$, being basically the Fourier transform of a well-behaved function. Hence, in this approximation of using product wave functions for $|m\rangle$ the dispersion interaction is finite at $R\to 0$ to all orders of multipolarity. Thus, this formalism includes results of Richardson[2]—in fact, one can get term-by-term correspondence with Richardson's multipolar terms by taking (2.7), expanding one $f_{mn}(\vec{k})$ in a power series in k, and retaining the other as such in each of the two terms in the right-hand side and using that in (2.11). The limit $R\to 0$ is, of course, only of academic interest since exchange effects will dominate at small R and the approximation of taking product wave functions for $|m\rangle$ will break down.

If instead of product wave functions, properly antisymmetrized wave functions are used for $|m\rangle$, $D_{ll'}(\vec{k},\vec{k}';\omega)$ for $l\neq l$ will not vanish identically. We will then get for $V(R)$ in (2.11) nonvanishing contributions in the first order in (e^2); but these contributions will always be of the short range type, containing exponentially decaying functions of R, which arise from the exchange integrals.

IV. AN EXAMPLE

As an illustration of the above formalism we consider the case of two hydrogen atoms in their ground states, and we shall take product wave functions for the excited states.

Thus,

$$|n\rangle=|0\rangle\equiv\psi^{(1)}_{1s}(\vec{r}_{(1)})\psi^{(2)}_{1s}(\vec{r}_{(2)})\,. \tag{4.1}$$

The excited states can be written in terms of hydrogen wave functions; but for simplicity we shall estimate the sum over the intermediate states in (3.1) by taking an average energy denominator, as is customary in such problems. We can thus write, using (2.8),

$$\sum_m\left(\frac{[f^{(1)}_{m0}(\vec{k})]^*[f^{(1)}_{m0}(\vec{k}')]}{E_0-E_m+\hbar\omega}+\frac{[f^{(1)}_{0m}(\vec{k})]^*[f^{(1)}_{0m}(\vec{k}')]}{E_0-E_m-\hbar\omega}\right)$$
$$\approx\frac{2(E_0-\overline{E}_m)}{(E_0-\overline{E}_m)^2-(\hbar\omega)^2}\left(\langle\psi_{1s}|e^{-i(\vec{k}-\vec{k}')\cdot\vec{r}}\psi_{1s}\rangle-\langle\psi_{1s}|e^{-i\vec{k}\cdot\vec{r}}|\psi_{1s}\rangle\langle\psi_{1s}|e^{i\vec{k}'\cdot\vec{r}}|\psi_{1s}\rangle\right)$$
$$=\left(\frac{2E_a}{E_a^2-(\hbar\omega)^2}\right)[k_0^4]\left(\frac{1}{[k_0^2+(\vec{k}-\vec{k}')^2]^2}-\frac{k_0^4}{(k_0^2+k^2)^2(k_0^2+k'^2)^2}\right). \tag{4.2}$$

Here $k_0 = (2/a_0)$, a_0 being the Bohr radius. This approximation, which is equivalent to having a dominant oscillator strength at the frequency $(E_a/2\hbar)$, also preserves the properties of the above sum that it vanishes for $\vec{k} = \vec{k}' = 0$, and for $(\vec{k}, \vec{k}') \rightarrow \infty$. Substituting this in (3.1) we get,

$$V(R) = -\left(\frac{1}{2E_a}\right)\left(\frac{4\pi e^2}{V}\right)^2 \sum_{\vec{k},\vec{k}'} \frac{k_0^8}{k^2 k'^2} \times \left(\frac{1}{[k_0^2 + (\vec{k}-\vec{k}')^2]^2} - \frac{k_0^4}{(k_0^2+k^2)^2(k_0^2+k'^2)^2}\right) \times e^{-i(\vec{k}-\vec{k}')\cdot\vec{R}} . \tag{4.3}$$

Although this expression is an approximation, it contains the various size effects we have discussed in Sec. III. For $R \rightarrow 0$, $V(R)$ goes to the finite limit

$$\lim_{R \rightarrow 0} V(R) = -\left(\frac{355}{1728}\right)\left(\frac{e^4}{a_0^2}\right)\frac{1}{2E_a} . \tag{4.4}$$

For large R we get the asymptotic series

$$V(R) \approx -\left(\frac{e^4}{a_0^2}\right)\left(\frac{1}{2E_a}\right)\left[6\left(\frac{a_0}{R}\right)^6 + 199\left(\frac{a_0}{R}\right)^8 + \cdots\right] . \tag{4.5}$$

This is the usual multipolar series for Van der Waals interaction.

V. CONCLUSION

The main result we have is obtaining the Van der Waals interaction energy of two atoms in a compact form incorporating all the multipolar contributions. It is a well-behaved function for all values of the distance of separation R. Although this has been demonstrated in a simple example taking product wave functions, in principle this approach can be used, taking properly antisymmetrized wave functions, to yield the Van der Waals part of the interatomic potential exactly.

The effect of the finite size of the atomic charge distribution is taken into consideration in a natural way through the form factors $f_{mn}^{(l)}(\vec{k})$ defined in (2.8). Such form factors were taken into account phenomenologically in related problems earlier,[1,2] and they also occur in the problem of dispersion energy of an impurity in a dielectric[7,8] which is connected with the theory of a bound polaron.

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