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Dispersion forces between oscillators: a semi-classical treatment

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Abstract. It is shown that a semiclassical treatment of dispersion forces, based on the dependence of the zero point energy of two oscillators coupled to the electromagnetic field on their distance of separation gives the retarded and nonretarded form of the dispersion forces between them.

1. Introduction

The theory of dispersion forces between atoms and molecules has been investigated in great detail (Margenau and Kestner 1969) since London (1930a) gave his treatment of van der Waals forces. There are interesting physical features of the interaction of two molecules through their mutual coupling with the electromagnetic field which makes it possible to study the essential physics of the problem in a semiclassical framework. From this point of view, at the absolute zero of temperature the interaction is due to changes in the zero point energy of the coupled system as the distance between the molecules is altered. The electromagnetic field which causes the coupling can be treated classically, and we get the same result as had been obtained earlier by Casimir and Polder (1948) from consideration of the change of the zero point energy of the electromagnetic field. The object of this paper is to elaborate on this theme, taking the molecules as oscillators embedded in the electromagnetic field.

An oscillator in isolation has a sharp frequency, so that its frequency distribution function is a δ function. When it is coupled to a large assembly of oscillators, or in the continuum limit, to a field, the effect of the coupling is to convert the δ function into a spread-out spectral density function in a manner that can be computed in terms of the coupling constant and the spectrum of frequencies of the system to which it is coupled. This approach, for instance, is the basis of the 'pseudomolecular model' for the vibrations of impurities in crystals (Sachdev and Mahanty 1970).

The ground state energy of the oscillator (if it has more than one frequency) is given by

$$E_0 = \frac{\hbar}{2}\sum_j \omega_j = \frac{\hbar}{2}\frac{1}{2\pi \mathrm{i}}\int_C \omega \frac{\mathrm{d}\ln D_0(\omega)}{\mathrm{d}\omega}\,\mathrm{d}\omega \tag{1}$$

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where $D_0(\omega)$ is the secular determinant, and the contour C is so chosen as to include the positive real axis in the ω plane. The latter contour integral form is valid because $(\mathrm{d}/\mathrm{d}\omega)\ln D_0(\omega)$ has simple poles at the zeros of $D_0(\omega)$. When the oscillator is coupled to a field there will be a change in its secular determinant, and the difference

$$\Delta E_0 = \frac{\hbar}{2}\frac{1}{2\pi \mathrm{i}}\int_C \omega \frac{\mathrm{d}}{\mathrm{d}\omega}\ln\left(\frac{D_1(\omega)}{D_0(\omega)}\right)\mathrm{d}\omega \tag{2}$$

where $D_1(\omega)$ is the secular determinant in the coupled situation, is a measure of the selfenergy of the oscillator. When two such oscillators are coupled to the field, the interaction energy is the difference between the energy of the pair and the selfenergies of the two oscillators

$$E(1,2) = \frac{\hbar}{2}\frac{1}{2\pi \mathrm{i}}\int_C \omega \frac{\mathrm{d}}{\mathrm{d}\omega}\ln\left(\frac{D_{12}(\omega)}{D_1(\omega)D_2(\omega)}\right)\mathrm{d}\omega. \tag{3}$$

Here $D_2(\omega)$ and $D_{12}(\omega)$ are the secular determinants when the second oscillator is coupled to the field, and when both are coupled to the field respectively. Such formulae have been used in lattice dynamics to evaluate the interaction of a pair of impurities in a crystal (Maradudin *et al* 1963). An integration by parts and a suitable choice of the contour including the imaginary axis makes it possible to write equation (3) in the form

$$E(1,2) = \frac{\hbar}{2\pi \mathrm{i}}\int_0^{\mathrm{i}\infty} \ln \Omega(\omega)\,\mathrm{d}\omega. \tag{4a}$$

Here $\ln \Omega(\omega)$ is evaluated on the imaginary axis by analytic continuation of the function

$$\Omega(\omega) = \lim_{\epsilon\to 0^+}\left(\frac{D_{12}(\omega+\mathrm{i}\epsilon)}{D_1(\omega+\mathrm{i}\epsilon)D_2(\omega+\mathrm{i}\epsilon)}\right). \tag{4b}$$

Equation (4) will be the basis of the present treatment.

2. Formulation of the problem

Let us consider two identical three dimensional anisotropic oscillators, in each of which the oscillating particle is an electron, and there is a positively charged heavy core to keep the system electrically neutral. If A and Φ are the vector and scalar potentials of the electromagnetic field, the classical equations of motion are

$$\left(\mathbf{M}\frac{\mathrm{d}^2}{\mathrm{d}t^2}+\mathbf{V}\right)\boldsymbol{r}_1 = \frac{e}{c}\frac{\partial A(\boldsymbol{R}_1, t)}{\partial t}+e\nabla\Phi(\boldsymbol{R}_1, t) \tag{5a}$$

$$\nabla^2 A - \frac{1}{c^2}\frac{\partial^2 A}{\partial t^2} = \frac{4\pi e}{c}\left(\frac{\mathrm{d}\boldsymbol{r}_1}{\mathrm{d}t}\delta(\boldsymbol{r}-\boldsymbol{R}_1)+\frac{\mathrm{d}\boldsymbol{r}_2}{\mathrm{d}t}\delta(\boldsymbol{r}-\boldsymbol{R}_2)\right) \tag{5b}$$

$$\nabla . A + \frac{1}{c}\frac{\partial \Phi}{\partial t} = 0 \tag{5c}$$

$$\left(\mathbf{M}\frac{\mathrm{d}^2}{\mathrm{d}t^2}+\mathbf{V}\right)\boldsymbol{r}_2 = \frac{e}{c}\frac{\partial A(\boldsymbol{R}_2, t)}{\partial t}+e\nabla\Phi(\boldsymbol{R}_2, t). \tag{5d}$$

Here $\mathbf{M}$ and $\mathbf{V}$ are the mass and potential energy matrices of each oscillator, $\boldsymbol{R}_j$ is the equilibrium location and $\boldsymbol{r}_j$ the displacement from equilibrium of the jth oscillator, and the δ functions in equation (5*b*) demand that the particular solution of interest is to be obtained with the oscillators, regarded as points, at positions $\boldsymbol{R}_1$ and $\boldsymbol{R}_2$. Since we are interested in the distribution of the frequencies of the oscillators we take the Fourier time transform to obtain

$$(\mathbf{V}-\mathbf{M}\omega^2)\boldsymbol{u}_1(\omega) = \frac{\mathrm{i}\omega e}{c}\mathscr{A}(\boldsymbol{R}_1, \omega)+e\nabla\varphi(\boldsymbol{R}_1, \omega) \qquad (6a)$$

$$\left(\nabla^2+\frac{\omega^2}{c^2}\right)\mathscr{A}(\boldsymbol{r}, \omega) = \frac{4\pi\mathrm{i}\omega e}{c}\{\boldsymbol{u}_1(\omega)\delta(\boldsymbol{r}-\boldsymbol{R}_1)+\boldsymbol{u}_2(\omega)\delta(\boldsymbol{r}-\boldsymbol{R}_2)\} \qquad (6b)$$

$$\nabla\,.\,\mathscr{A}(\boldsymbol{r}, \omega)+\frac{\mathrm{i}\omega}{c}\varphi(\boldsymbol{r}, \omega) = 0 \qquad (6c)$$

$$(\mathbf{V}-\mathbf{M}\omega^2)\boldsymbol{u}_2(\omega) = \frac{\mathrm{i}\omega e}{c}\mathscr{A}(\boldsymbol{R}_2, \omega) + e\nabla\varphi(\boldsymbol{R}_2, \omega). \qquad (6d)$$

Here

$$\mathscr{A}(\boldsymbol{r}, \omega) = \frac{1}{\sqrt{(2\pi)}}\int_{-\infty}^{\infty}\mathscr{A}(\boldsymbol{r}, t)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t \qquad (7a)$$

$$\boldsymbol{u}_j(\omega) = \frac{1}{\sqrt{(2\pi)}}\int_{-\infty}^{\infty}\boldsymbol{r}_j(t)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t \qquad (7b)$$

$$\varphi(\boldsymbol{r}, \omega) = \frac{1}{\sqrt{(2\pi)}}\int_{-\infty}^{\infty}\Phi(\boldsymbol{r}, t)\exp(-\mathrm{i}\omega t)\,\mathrm{d}t. \qquad (7c)$$

To obtain the secular determinant for the two oscillators we solve for $\mathscr{A}(\boldsymbol{r}, \omega)$ from equation (6*b*)

$$\mathscr{A}(\boldsymbol{r}, \omega) = \frac{4\pi\mathrm{i}\omega e}{c}\{\boldsymbol{u}_1(\omega)\mathbf{G}(\boldsymbol{r}-\boldsymbol{R}_1\,;\omega)+\boldsymbol{u}_2(\omega)\mathbf{G}(\boldsymbol{r}-\boldsymbol{R}_2\,;\omega)\} \qquad (8)$$

where the Green function matrix $\mathbf{G}(\boldsymbol{r}-\boldsymbol{r}'\,;\omega)$ is

$$\mathbf{G}(\boldsymbol{r}-\boldsymbol{r}'\,;\omega) = \mathbf{I}\frac{1}{(2\pi)^3}\int\frac{\mathrm{d}^3k\exp\{\mathrm{i}\boldsymbol{k}\,.\,(\boldsymbol{r}-\boldsymbol{r}')\}}{\omega^2/c^2-k^2} \qquad (9)$$

and $\mathbf{I}$ is the unit matrix. Using equation (8), $\mathscr{A}$ and φ can be eliminated from equation (6*a*) and (6*d*), and the final result is

$$\left(\mathbf{V}-\mathbf{M}\omega^2+\frac{4\pi\omega^2e^2}{c^2}\mathbf{G}(\mathbf{0}\,;\omega)+4\pi e^2\{\nabla_r\nabla_r\mathbf{G}(\boldsymbol{r}-\boldsymbol{R}_1\,;\omega)\}_{\boldsymbol{r}=\boldsymbol{R}_1}\right)\boldsymbol{u}_1(\omega)$$
$$+\left(\frac{4\pi\omega^2e^2}{c^2}\mathbf{G}(\boldsymbol{R}\,;\omega)+4\pi e^2\{\nabla_r\nabla_r\mathbf{G}(\boldsymbol{r}-\boldsymbol{R}_2\,;\omega\}_{\boldsymbol{r}=\boldsymbol{R}_1}\right)\boldsymbol{u}_2(\omega) = 0 \qquad (10a)$$

$$\left(\mathbf{V}-\mathbf{M}\omega^2+\frac{4\pi\omega^2e^2}{c^2}\mathbf{G}(\mathbf{0}\,;\omega)+4\pi e^2\{\nabla_r\nabla_r\mathbf{G}(\boldsymbol{r}-\boldsymbol{R}_2\,;\omega)\}_{\boldsymbol{r}=\boldsymbol{R}_2}\right)\boldsymbol{u}_2(\omega)$$
$$+\left(\frac{4\pi\omega^2e^2}{c^2}\mathbf{G}(-\boldsymbol{R}\,;\omega)+4\pi e^2\{\nabla_r\nabla_r\mathbf{G}(\boldsymbol{r}-\boldsymbol{R}_1\,;\omega)\}_{\boldsymbol{r}=\boldsymbol{R}_2}\right)\boldsymbol{u}_1(\omega) = 0 \qquad (10b)$$

where $\boldsymbol{R} = \boldsymbol{R}_1-\boldsymbol{R}_2$.

The secular determinant is thus given by,

$$D_{12}(\omega) = \left\| \begin{bmatrix} \left(\mathsf{V}-\mathsf{M}\omega^2+\frac{4\pi\omega^2 e^2}{c^2}\mathsf{G}(\mathbf{0};\omega)+4\pi e^2\mathscr{G}(\mathbf{0};\omega)\right) & \left(\frac{\omega^2}{c^2}\mathsf{G}(\boldsymbol{R};\omega)+\mathscr{G}(\boldsymbol{R};\omega)\right)4\pi e^2 \\ \left(\frac{\omega^2}{c^2}\mathsf{G}(-\boldsymbol{R};\omega)+\mathscr{G}(-\boldsymbol{R};\omega)\right)4\pi e^2 & \left(\mathsf{V}-\mathsf{M}\omega^2+\frac{4\pi\omega^2 e^2}{c^2}\mathsf{G}(\mathbf{0};\omega)+4\pi e^2\mathscr{G}(\mathbf{0};\omega)\right) \end{bmatrix} \right\| \tag{11}$$

where

$$\mathscr{G}(\boldsymbol{r}-\boldsymbol{r}';\omega) = \nabla_r\nabla_r\mathsf{G}(\boldsymbol{r}-\boldsymbol{r}';\omega). \tag{12}$$

In this case $D_1(\omega)$ and $D_2(\omega)$ both have the form

$$D_1(\omega) = D_2(\omega) = \left\|\left(\mathsf{V}-\mathsf{M}\omega^2+\frac{4\pi\omega^2 e^2}{c^2}\mathsf{G}(\mathbf{0};\omega)+4\pi e^2\mathscr{G}(\mathbf{0};\omega)\right)\right\|. \tag{13}$$

We thus have

$$\begin{aligned}\frac{D_{12}(\omega)}{D_1(\omega)D_2(\omega)} = \Bigg|\Bigg\{\mathsf{I}-16\pi^2 e^4\left(\mathsf{V}-\mathsf{M}\omega^2+\frac{4\pi e^2\omega^2}{c^2}\mathsf{G}(\mathbf{0};\omega)+4\pi e^2\mathscr{G}(\mathbf{0};\omega)\right)^{-1} \\ \times\left(\frac{\omega^2}{c^2}\mathsf{G}(-\boldsymbol{R};\omega)+\mathscr{G}(-\boldsymbol{R};\omega)\right)\times\bigg(\mathsf{V}-\mathsf{M}\omega^2+\frac{4\pi e^2\omega^2}{c^2}\mathsf{G}(\mathbf{0};\omega) \\ +4\pi e^2\mathscr{G}(\mathbf{0};\omega)\bigg)^{-1}\times\left(\frac{\omega^2}{c^2}\mathsf{G}(\boldsymbol{R};\omega)+\mathscr{G}(\boldsymbol{R};\omega)\right)\Bigg\}\Bigg|.\end{aligned} \tag{14}$$

If we are interested in terms of order (e^4), we obtain

$$\begin{aligned}\ln\left[\frac{D_{12}(\omega)}{D_1(\omega)D_2(\omega)}\right] \simeq -16\pi^2 e^4\,\mathrm{Tr}\Bigg\{(\mathsf{V}-\mathsf{M}\omega^2)^{-1}\times\left(\frac{\omega^2}{c^2}\mathsf{G}(-\boldsymbol{R};\omega)+\mathscr{G}(-\boldsymbol{R};\omega)\right) \\ \times\{\mathsf{V}-\mathsf{M}\omega^2\}^{-1}\times\left(\frac{\omega^2}{c^2}\mathsf{G}(\boldsymbol{R};\omega)+\mathscr{G}(\boldsymbol{R};\omega)\right)\Bigg\}.\end{aligned} \tag{15}$$

Using this in equation (4) we get (with the substitution $\omega = \mathrm{i}\xi$)

$$\begin{aligned}E(1,2) \equiv E(R) = -\frac{\hbar}{2\pi}(16\pi^2 e^4)\int_0^\infty \mathrm{d}\xi\,\mathrm{Tr}\Bigg\{(\mathsf{V}+\mathsf{M}\xi^2)^{-1} \\ \times\left(\frac{\xi^2}{c^2}\mathsf{G}(-\boldsymbol{R};\mathrm{i}\xi)-\mathscr{G}(-\boldsymbol{R};\mathrm{i}\xi)\right)\times(\mathsf{V}+\mathsf{M}\xi^2)^{-1} \\ \times\left(\frac{\xi^2}{c^2}\mathsf{G}(\boldsymbol{R};\mathrm{i}\xi)-\mathscr{G}(\boldsymbol{R};\mathrm{i}\xi)\right)\Bigg\}.\end{aligned} \tag{16}$$

3. The isotropic oscillator—retarded and nonretarded limits

To get the essential physics from this point on we simplify the problem by assuming that the oscillators are isotropic, so that $(\mathsf{V}+\mathsf{M}\xi^2)$ is a scalar matrix

$$\mathsf{V}+\mathsf{M}\xi^2 \equiv m(\omega_0^2+\xi^2)\mathsf{I}. \tag{17}$$

Also

$$\mathbf{G}(\pm\boldsymbol{R};\mathrm{i}\xi) = -\mathsf{I}\frac{\exp(-\xi R/c)}{4\pi R} \tag{18}$$

and

$$\mathscr{G}(\pm\boldsymbol{R};\mathrm{i}\xi) = \frac{\exp(-\xi R/c)}{4\pi R}\begin{bmatrix} \left(\frac{1}{R^2}+\frac{\xi}{cR}\right) & 0 & 0 \\ 0 & \left(\frac{1}{R^2}+\frac{\xi}{cR}\right) & 0 \\ 0 & 0 & -\left(\frac{\xi^2}{c^2}+\frac{2\xi}{cR}+\frac{2}{R^2}\right) \end{bmatrix}. \tag{19}$$

Hence, equation (16) becomes

$$E(R) = -\frac{\hbar}{2\pi}\frac{e^4}{m^2R^2}\int_0^\infty \frac{\mathrm{d}\xi\,\exp(-2\xi R/c)}{(\omega_0^2+\xi^2)^2}\left\{2\left(\frac{\xi^2}{c^2}+\frac{\xi}{cR}+\frac{1}{R^2}\right)^2+4\left(\frac{\xi}{cR}+\frac{1}{R^2}\right)^2\right\}. \tag{20}$$

The nonretarded limit is obtained when $c \to \infty$, and in that case

$$E(R) = -\frac{\hbar}{2\pi}\frac{e^4}{m^2R^6}6\int_0^\infty \frac{\mathrm{d}\xi}{(\omega_0^2+\xi^2)^2} = -\frac{3\hbar e^4}{4m^2\omega_0^3R^6}. \tag{21}$$

This is the London (1930*b*) limit.

In the retarded case, with a substitution $\xi R/c = x$, equation (20) becomes

$$E(R) = -\frac{\hbar c e^4}{\pi m^2 R^7}\int_0^\infty \frac{\mathrm{d}x\,\exp(-2x)}{\{\omega_0^2+(x^2c^2/R^2)\}^2}(x^4+2x^3+5x^2+6x+3). \tag{22}$$

This admits of an asymptotic series expansion in powers of $1/R$, but the leading term is

$$E(R) = -\frac{23\hbar c}{4\pi R^7}\frac{e^4}{m^2\omega_0^4}. \tag{23}$$

This is essentially the Casimir–Polder result (Casimir and Polder 1948), when $(e^4/m^2\omega_0^4)$ is identified with the product of the static polarizabilities of the two oscillators.

The complete expression for the interaction energy in this semiclassical approach is given by

$$E(R) = \frac{\hbar}{2\pi}\int_0^\infty \mathrm{d}\xi\left\{2\ln\left(1-\frac{e^4}{R^2}\frac{\{(1/R^2)+(\xi/cR)+(\xi^2/c^2)\}^2\exp(-2\xi R/c)}{\{m(\omega_0^2+\xi^2)+(2e^2\xi^3/3c^3)\}^2}\right)\right.$$
$$\left.+\ln\left(1-\frac{4e^4}{R^2}\frac{\{(\xi/cR)+(1/R^2)\}^2\exp(-2\xi R/c)}{\{m(\omega_0^2+\xi^2)+(2e^2\xi^3/3c^3)\}^2}\right)\right\}. \tag{24}$$

A point of interest is that selfenergy of a single oscillator given in equation (2) diverges, even though the interaction energy of two oscillators given in equation (3) converges. The divergence of the selfenergy term is well known in quantum electrodynamics; such a divergence does not occur in the corresponding problem in lattice dynamics because of the nature of the dispersion law in a lattice which provides an upper bound to the frequencies. However, even though the selfenergy diverges, it is possible to obtain an intensity distribution formula for the radiation from the oscillator which will be damped because of radiation from it. This formula is merely the frequency distribution function of the oscillator when it is coupled to the electromagnetic field, and can be obtained from equation (13). Thus

$$I(\omega) = \frac{I_0}{\pi} \operatorname{Im} \frac{\mathrm{d}}{\mathrm{d}\omega} \ln D_1(\omega)|_{\omega - \mathrm{i}0^+} = \frac{I_0}{\pi} \frac{\mathrm{d}}{\mathrm{d}\omega} P(\omega) \tag{25}$$

where

$$P(\omega) = \tan^{-1}\left(\frac{\operatorname{Im} D_1(\omega - \mathrm{i}0^+)}{\operatorname{Re} D_1(\omega - \mathrm{i}0^+)}\right) \tag{26}$$

and I_0 is so chosen as to normalize the distribution function. The calculations can be completed trivially and the result in the isotropic case is

$$I(\omega) = I_0 \frac{6e^2}{3\pi mc^3} \frac{3\omega^2\omega_0^2 - \omega^4}{(\omega_0^2 - \omega^2)^2 + (2e^2\omega^3/3mc^3)^2}. \tag{27}$$

For ω in the neighbourhood of ω_0 the above expression reduces to

$$I(\omega) \simeq I_0 \frac{3}{2\pi}\left(\frac{2e^2\omega_0^2}{3mc^3}\right) \frac{1}{(\omega_0 - \omega)^2 + \frac{1}{4}(2e^2\omega_0^2/3c^3m)^2}. \tag{28}$$

This can be compared with the well known radiation damping formula of an oscillator (Heitler 1954) where the damping constant is given by

$$\Gamma = \frac{2e^2\omega_0^2}{3mc^3}. \tag{29}$$

The factor 3 in equation (28) arises because we have three identical oscillators in this model.

In conclusion, it is interesting to evaluate the range of values of R for which the non-retarded limit holds. It may be noted from equation (11) and the small R behaviour of the Green functions in equations (18) and (19) that the splitting of the oscillator frequencies is of the order of (e^2/R^3). The natural line width is of the order of $e^2\omega_0^3/c^3$. Hence, if the splitting is more than the natural line width, that is, if $R < c/\omega_0$ the splitting will predominate and London's nonretarded treatment will be valid. This, of course, is the same condition as the one stated by Casimir and Polder on the ground that if $R > c/\omega_0$, the retardation effect will predominate, although the approach here is somewhat different. The expression for the interaction energy given in equation (24) is formally similar to that given by Mitchell *et al* (1972) from a different point of view, for the interaction energy between two molecules.

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