THE EFFECTS OF BOUNDARIES ON THE DISPERSION FORCES BETWEEN MOLECULES

A thesis submitted for the degree of Master of Science at the Australian National University

by

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STATEMENT

I hereby declare that to the best of my knowledge, no work previously written or published has been used in this thesis except where referenced in the text.

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ABSTRACT

Using semi-classical techniques a general theory is developed which enables us to study the effects of physical boundaries on the dispersion interaction between molecules taken as point dipole oscillators. The formalism is then applied to situations in which the oscillators are between metallic plates, in a metallic duct and then in a dielectric slab. The resonance interaction is also considered. It is found that in some instances the interaction is considerably altered from the London and Casimir-Polder results for free space.

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CHAPTER 1

The intermolecular forces between uncharged atoms and molecules generally fall into one of three basic types, orientation effect forces, induction effect forces, and dispersion forces.

'Orientation effect' forces arise when two molecules each possessing a permanent dipole attract each other due to the attraction between their dipoles when in certain orientations. Boltzmann statistics says that the orientations of lower energy are statistically preferred, the preference increasing as the temperature is lowered. Averaging over all positions an attractiv force is found as a result of this preference.

Forces due to the 'Induction effect' are once again attractive forces resulting from attraction between two molecules, one of which possesses a permanent dipole, the other being polarised by this dipole giving rise to an induced dipole (which may be in addition to any permanent dipole) and hence an attraction between them. At the same time, if the second molecule also possesses a permanent dipole it may be inducing a moment in the first to give rise to a further attractive contribution.

Debye [1] and Keesom [2] were the principal early workers in this field, their work mainly being as an attempt to determine theoretically the attractive constant in the Van der Waals gas equation due to intermolecular attraction. The 'Induction effect' calculation arose when it was found that the 'Orientation effect' could not be the only explanation as it did not possess the correct temperature dependence. For those molecules which obviously had no permanent dipole moment (e.g. rare gases, N_2, H_2, CH_4, O_2 etc.) the existence of quadrupole moments was assumed which would give a similar interaction by inducing dipoles in each other. As there was no other method available at the time to measure these quadrupoles they were determined backwards from the empirical Van der Waals gas equation constants.

However, with the development of Quantum Mechanics it was shown that the rare gases were spherically symmetric and so possessed no permanent dipole or other multipole. In the case of the homonuclear diatomics it was found that they possessed at least a permanent quadrupole. When this quadrupole was calculated for H_2 it was found to give rise to a Van der Waals force about one percent of that which had previously been attributed to a suitably chosen quadrupole.

On the other hand Quantum Mechanics also provided a new aspect of the interaction between neutral atomic systems. In 1930 London [3] using the Drude-Lorentz model [4] of the atom, which considers the atom to be an assembly of harmonic oscillators, calculated the force between such atoms which arose due to the interaction of their rapidly fluctuating instantaneous dipole moments. This force, again attractive was termed the Dispersion Force since it involved in the expression for the energy, terms related to Classical Dispersion Theory. This type of force first appeared in a calculation by Wang [5] who solved the Schrodinger equation for two hydrogen atoms at large separation distances, including the instantaneous dipole interaction between the stationary protons and moving electrons. For his calculation Wang used a rather cumbersome perturbation method developed by Epstein [6]. London [3] in his calculation, however, used a more standard Second order perturbation procedure to obtain his result.

In the early years following London's work this was the principal technique used, generally coupled with variational techniques, in calculating the Dispersion Forces. In the case of hydrogen atoms, Pauling and Beach [7] used a total of some sixty-nine terms for the dipole-dipole, dipole-quadrupole and quadrupole-quadrupole parts of the interaction to gain the first three terms in the series expansion for the energy of the interaction to a slightly greater accuracy than had been obtained by Margenau [8] some years earlier. These calculations were principally concerned with obtaining numerical answers for a specific substance.

Another approach adopted by some early workers [9] was to write the energy as

$$E = -C/R^6$$

and try to derive generally applicable formulae for C which agreed with the cases for which exact values could be measured and simultaneously gave some insight into the physical properties of the atom that were important in the magnitude of the interaction.

In the mid 1940's Verwey and Overbeek [10] developed a theory in which the interaction between colloidal particles was exclusively ascribed to Dispersion Forces and when applying it to suspensions of comparatively large particles they found a discrepancy between their theory and the experimental results which could only be resolved if the Dispersion Force between two atoms was assumed to fall off faster than R^{-7} (i.e. the energy of the interaction falling faster than R^{-6}). Overbeek then pointed out that given the idea of Dispersion Forces as being an interaction between instantaneous dipoles in the two atoms and hence carried by the electromagnetic field that retardation due to the finite speed of light might become important at distances comparable to the wavelengths of atomic frequencies. Inspired by this suggestion Casimir and Polder [11] using Quantum Electrodynamics found that for large separation distances the Dispersion Force energy fell off as R^{-7}.

Increasing refinement in the theory and techniques of Quantum Mechanics and Quantum Electrodynamics has seen the derivation of the energy of the Dispersion interaction by several different techniques, each starting from a slightly different assumption as to the process involved.

Fienberg and Sucher [12] using methods similar to those of Casimir and Polder have obtained a general form for the retarded dispersion force potential. In a later paper [13], by treating the interaction as being the exchange of two virtual photons between neutral spinless systems, they were able to express the energy of the interaction entirely in terms of measurable quantities, namely the elastic scattering amplitudes for photons of frequency w.

The time-dependent Hartree method was used by McLachlan, Gregory and Ball [14] to solve the problem of interacting atoms quantum mechanically, by-passing knowledge of the wave functions of the atoms concerned by using the frequency dependent polarisabilities [15]. These polarisabilities were then approximated using the time-dependent Hartree method. This method also enabled them to obtain a simple description of the non-additive three body forces and other extensions of the basic ideas, including temperature effects.

The problem was also attacked by Tang [16] using the dynamic polarisabilities. In the two earlier papers he approximated the polarisabilities by using a two-point Pade approximant. Using this he was then able to obtain the form for the two-body force previously obtained by Slater and Kirkwood [9] while for three-body forces he reproduced the results of Midzuno and Kihara [17]. In the later paper he used a continued factorisation method for approximating the polarisabilities thereby gaining tighter bounds than with the Pade approximant.

A totally different aspect of the problem has been considered by Boehm and Yaris [18]. In their paper they considered the small separation distance part of the problem, specifically the area in which orbital overlap becomes important and hence the force between the atoms tends to become repulsive. The complexity of the problem was somewhat reduced by their use of linear response methods from Quantum Mechanics.

The interaction between charged particles located between conducting plates, a problem which is a forerunner of a situation to be considered in this present work, was considered in 1970 by Barton [19] using Quantum Electrodynamics. He found that for the two particle interaction, the energy of the system including the charged particles arose from the coupling of the charged particles to the quantized electromagnetic field, thereby altering the energy of the quantized field.

Most of the methods of attack on the problem so far mentioned have been essentially of a quantum-mechanical nature using ideas and techniques developed principally since the rise of Quantum Theory around the 1920's. Several excellent reviews by Margenau and Kestner [20], Power[21] and Dalgarno and Davison [22] have been written on the Quantum theoretical development of the theory of intermolecular forces as well as a non-technical review by Winterton [23], these reviews giving a complete quantum treatment of intermolecular forces for the interested reader. See also the reviews of Israelachvili, [46] and of Parsegian, [45] who emphasise applications in biology.

More recent years have seen the rise of a different line of attack on the theory of intermolecular forces, the semi-classical approach. Any quantum treatment of the theory, by its very nature, tends to become rather complicated for even simple problems, and exact functional representations for many basic functions used (wave functions etc.) are not known and hence perturbation or other approximating techniques are used. The semi-classical approach, on the other hand, with its heavy flavouring of classical equations and techniques is basically much simplar to use, being able to draw on the vast body of classical theory already known.

An early use of classical ideas was by Lifshitz [24] in his work on the dispersion forces between continuous media and its later expansion [25] giving the well known Lifshitz theory for forces between continuous media. This work was based on macroscopic electrodynamic and fluctuation analysis. It is interesting to note that it was some many years before Renne and Nijboer [26, 27] were able to give an atomistic derivation of this macroscopic theory.

In an early paper, Boyer [28] expounded the connection between Quantum Mechanics as represented in the work by London [3] and Casimir and Polder [11] and Classical Electrodynamcis of fluctuating fields, the work of Lifshitz [24]. In a later series of papers [29], Boyer then went on to give a recalculation of the long range dispersion force potentials using Maxwell's equations for the electrodynamic field and classical electrodynamics.

Combining classical ideas and the quantum concept of zero-point energy, Van Kampen et al [30] achieved an important result when they showed how the energy of the intermolecular force may be calculated from a 'Dispersion Relation', a relation which determined the frequencies of the coupled atomic oscillators This work was at first applicable to non-dispersive media [31] but was later shown to be applicable to dispersive media as well [32].

A completely general theoretical treatment of the dispersion interaction was gained using the semi-classical approach by Mitchell et al [33] which gave both the repulsive limit mentioned earlier as well as the London [3] and Casimir and Polder [11] results as certain limiting cases, the method also being used to give an exact solution for the three body forces.

It is the semi-classical approach which we adopt in this work in determining the boundary effects on dispersion forces. Dispersion Force theory has in recent times been carried into many and varied fields as their importance in physical phenomena has been realised. We have already mentioned the application to the theory of colloids [10, see also 34] where Dispersion forces play a major part.

The Physical Adsorption process is another area in which dispersion forces play a major part, the adsorption process being governed by the dispersion forces within and between the various constituent parts. Two very good dissertations on the subject have been written by Young and Crowell [35] and De Boer [36] to which the interested reader is referred.

As Dispersion Force theory is carried into wider applications it becomes increasingly important to know how the dispersion interaction changes according to the environment of the problem at hand. It is one aspect of this problem that we look at in this work, namely that of how the dispersion forces between molecules taken as point dipole oscillators vary according to the boundaries of their physical environment.

In the first part of this work we develop the theory of interacting molecules in the manner outlined by Mahanty and Ninham [37, 38] and consider their application of it to a simple system and then in the later parts consider its application to slightly more complex configurations.

CHAPTER 2

The problem of interacting molecules has a simple formulation when set up in semi-classical terms [37]. For this formulation we regard the molecules as being point-dipole oscillators, mutually coupled via the electromagnetic field which is treated classically. The dispersion energy is then the difference in zero-point energy between the coupled oscillator system and that of two individual non-coupled oscillators. The boundary effects enter through the structure of the Green function of the electromagnetic field coupling the oscillators.

For an oscillator of a single frequency, its zero-point energy is given by

$$E = \tfrac{1}{2}\hbar\omega \tag{2.1}$$

where w is the circular frequency. If the ground state of the molecule is an assembly of oscillators of frequency w_j [27] then the zero-point energy of the molecule is given by

$$E_0 = \frac{\hbar}{2}\sum_j \omega_j \tag{2.2}$$

If $D_0(w)$ is the secular determinant for the molecule i.e. $D_0(w_j) = 0$ all j, then using Complex Variable Theory [39] we can write

$$E_0 = \frac{\hbar}{2}\cdot\frac{1}{2\pi i}\int_c d\omega\, \omega\, \frac{D_0'(\omega)}{D_0(\omega)} \tag{2.3}$$

$$= \frac{\hbar}{2}\cdot\frac{1}{2\pi i}\int_c \omega \frac{d}{dw}(\ln D_0(\omega))\, d\omega$$

since $D_0'(w)/D_0(w)$ has simple poles at the zeros of $D_0(w)$. The contour C in the complex-w plane is chosen so as to include the positive real axis.

If the oscillator is now coupled to the electromagnetic field, there will be a change in the secular determinant, the difference

$$\Delta E_0 = \frac{\hbar}{2}\cdot\frac{1}{2\pi i}\int_C \omega \frac{d}{d\omega}\left\{\ln \frac{D_1(\omega)}{D_0(\omega)}\right\} d\omega \tag{2.4}$$

where $D_1(w)$ is the secular determinant of the coupled situation, being a measure of the self-energy of the oscillator.

Now if we couple the two oscillators to the field, the interaction energy is the difference between the energy of the pair and the individual self-energies of the two oscillators

$$E(1,2) = \frac{\hbar}{2}\cdot\frac{1}{2\pi i}\int_c \omega \frac{d}{d\omega}\left\{\ln\left(\frac{D_{12}(\omega)}{D_1(\omega)D_2(\omega)}\right)\right\} d\omega \tag{2.5}$$

In equation (2.5) $D_2(w)$ is the secular determinant for the second oscillator coupled to the field and $D_{12}(w)$ the secular determinant for both oscillators coupled to the field.

Integrating equation (2.5) by parts and choosing a contour including the imaginary axis we obtain

$$E(1,2) = \frac{\hbar}{2\pi i}\int_0^{i\infty} \ln \Omega(\omega)\, d\omega \tag{2.6}$$

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

$$\Omega(\omega) = \lim_{\epsilon\to 0^+}\left(\frac{D_{12}(\omega+i\epsilon)}{D_1(\omega+i\epsilon)\,D_2(\omega+i\epsilon)}\right) \tag{2.7}$$

Equation (2.6) is one of the results on which we base our treatment.

We now turn our attention to the equations of motion of two isotropic oscillators [38], natural frequency w , charge (-e) and mass m. In Fourier Transform (time-independent) form these are

$$m(\omega_0^2 - \omega^2)\, \underset{\sim}{u}_j(\omega) = \frac{i\omega e}{c} \underset{\sim}{A}(\underset{\sim}{R}_j, \omega) + e \nabla\phi(\underset{\sim}{R}_j, \omega) \qquad j = 1, 2 \qquad (2.8)$$

where $\underset{\sim}{u}_j$ is the displacement from equilibrium of the jth oscillator, and $\underset{\sim}{R}_j$ the co-ordinates of its equilibrium position and also that of the core positive charge (+e), assumed to be stationary.

The time-independent equations for the vector and scalar potentials $\underset{\sim}{A}$ and ϕ are (using Coulomb gauge)

$$\left(\nabla^2 + \frac{\omega^2}{c^2}\right) \underset{\sim}{A}(\underset{\sim}{r}, \omega) = \frac{i\omega}{c} \nabla\phi + \frac{4\pi i\omega e}{c} \sum_j \underset{\sim}{u}_j(\omega)\, \delta(\underset{\sim}{r}, \underset{\sim}{R}_j) \qquad (2.9)$$

$$\nabla . \underset{\sim}{A} = 0 \qquad (2.10)$$

and

$$\nabla^2 \phi = 4\pi e \sum_j \left\{ \nabla_{R_j} \delta(\underset{\sim}{r}, \underset{\sim}{R}_j) . \underset{\sim}{u}_j(\omega) \right\} \qquad (2.11)$$

Solving for $\underset{\sim}{A}$ and ϕ from equations (2.9), (2.10) and (2.11) in terms of $G^{(1)}(\underset{\sim}{r}, \underset{\sim}{r}')$, the Green function of

$$\nabla^2 \phi = 0 \qquad (2.12)$$

and $\underset{=}{G}^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}', w)$ the diadic Green function of

$$\left(\nabla^2 + \frac{\omega^2}{c^2}\right) \underset{\sim}{A} = 0 \qquad (2.13)$$

with the appropriate boundary conditions, we obtain on substitution into equations (2.8)

$$\left[m(\omega_0^2-\omega^2)\underline{\underline{I}} + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_1, \underset{\sim}{R}_1;\omega)\right]\underset{\sim}{u}_1 + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_1, \underset{\sim}{R}_2;\omega)\underset{\sim}{u}_2 = 0 \tag{2.14}$$

$$\left[m(\omega_0^2-\omega^2)\underline{\underline{I}} + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_2, \underset{\sim}{R}_2;\omega)\right]\underset{\sim}{u}_2 + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_2, \underset{\sim}{R}_1;\omega)\underset{\sim}{u}_1 = 0 \tag{2.15}$$

Here $\underline{\underline{I}}$ is the unit diadic and

$$\underline{\underline{G}}(\underset{\sim}{r}, \underset{\sim}{r}';\omega) = \frac{\omega^2}{c^2}\underline{\underline{G}}^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}';\omega) - \nabla\nabla' G^{(1)}(\underset{\sim}{r}, \underset{\sim}{r}') \tag{2.16}$$

with $\nabla\nabla'$ the diadic operator formed from the gradient operators for primed and unprimed co-ordinates.

Hence from equations (2.14) and (2.15) we have the secular determinant for the coupled system as

$$D_{12}(\omega) = \begin{vmatrix} m(\omega_0^2-\omega^2)\underline{\underline{I}} + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_1, \underset{\sim}{R}_1;\omega) & 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_1, \underset{\sim}{R}_2;\omega) \\ 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_2, \underset{\sim}{R}_1;\omega) & m(\omega_0^2-\omega^2)\underline{\underline{I}} + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_2, \underset{\sim}{R}_2;\omega) \end{vmatrix} \tag{2.17}$$

and also

$$D_j(\omega) = \left| m(\omega_0^2-\omega^2)\underline{\underline{I}} + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_j, \underset{\sim}{R}_j;\omega) \right| \tag{2.18}$$

Therefore we have that

$$\frac{D_{12}(\omega)}{D_1(\omega)D_2(\omega)} = \Big| \underline{\underline{I}} - 16\pi^2 e^4 \underline{\underline{G}}(\underset{\sim}{R}_2, \underset{\sim}{R}_1;\omega) \times \left[m(\omega_0^2-\omega^2)\underline{\underline{I}} + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_2, \underset{\sim}{R}_2;\omega)\right]^{-1} \times \underline{\underline{G}}(\underset{\sim}{R}_1, \underset{\sim}{R}_2;\omega) \times \left[m(\omega_0^2-\omega^2)\underline{\underline{I}} + 4\pi e^2 \underline{\underline{G}}(\underset{\sim}{R}_1, \underset{\sim}{R}_1;\omega)\right]^{-1} \Big| \tag{2.19}$$

So to order (e^4) we obtain

$$\ln\left(\frac{D_{12}(\omega)}{D_1(\omega)\,D_2(\omega)}\right) \approx \frac{-16\pi^2 e^4}{m(\omega_0^2-\omega^2)^2}\,\mathrm{Tr}\left\{\underline{\underline{G}}(\underline{R}_1,\underline{R}_2;\omega)\cdot\underline{\underline{G}}(\underline{R}_2,\underline{R}_1;\omega)\right\} \qquad (2.20)$$

Substituting equation (2.20) into equation (2.6) in the form

$$E(R) = \frac{-\hbar}{4\pi i}\int_{i\infty}^{-i\infty} \ln\left\{\frac{D_{12}(\omega)}{D_1(\omega)\,D_2(\omega)}\right\} d\omega \qquad (2.21)$$

and writing $w = i\xi$ we then have

$$E(R) \approx -\frac{8\pi^2\hbar e^4}{m^2}\int_0^{\infty}\frac{d\xi}{(\omega_0^2+\xi^2)^2}\,\mathrm{Tr}\left(\underline{\underline{G}}(\underline{R}_1,\underline{R}_2;i\xi)\cdot\underline{\underline{G}}(\underline{R}_2,\underline{R}_1;-i\xi)\right) \qquad (2.22)$$

The use of the Coulomb gauge enables us to separate out the non-retarded form of $\underline{\underline{G}}(\underline{r},\underline{r}';\omega)$ in equation (2.22). Therefore in the non-retarded limit with $c \to \infty$, equation (2.22) becomes

$$E(R) = \frac{-2\pi^2\hbar e^4}{m^2\omega_0^3}\,\mathrm{Tr}\left\{\left[\nabla_{R_1}\nabla_{R_2}G^{(i)}(\underline{R}_1,\underline{R}_2)\right]\left[\nabla_{R_2}\nabla_{R_1}G^{(i)}(\underline{R}_2,\underline{R}_1)\right]\right\} \qquad (2.23)$$

Equations (2.22) and (2.23) will form the basis for further analysis.

CHAPTER 3

3.1 The Green Functions

We see from equations (2.22) and (2.23) that the energy of the interaction is dependent on the Green function of the problem configuration. In bounded regions the structure of the Green function is altered by the discretization of some, or in some cases all, of the modes of the electromagnetic field in the bounded region. The actual boundary conditions to be used depend on the physical nature of the boundary (metal, dielectric etc.) and may involve physical properties of the boundary such as dielectric constant, electrical conductivity etc.

For the problem of the oscillators between perfectly conducting metallic walls it is advantageous to use an eigenfunction expansion for the two Green functions $G^{(1)}(\underline{r},\underline{r}')$ and $\underline{\underline{G}}^{(2)}(\underline{r},\underline{r}';\omega)$, the general theory being well known [40].

In an eigenfunction expansion then, $G^{(1)}(\underline{r},\underline{r}')$ of equation (2.12) is constructed from the solutions of the scalar equation

$$\nabla^2 \chi_\lambda(\underline{r}) = \lambda\, \chi_\lambda(\underline{r}) \qquad (3.1)$$

where χ_λ is suitably normalised and is chosen to satisfy the same boundary conditions as ϕ. Using the χ_λ we then have

$$G^{(1)}(\underline{r},\underline{r}') = \sum_\lambda \frac{\chi_\lambda(\underline{r})\,\chi^*_\lambda(\underline{r}')}{\lambda} \qquad (3.2)$$

We obtain the diadic Green function $\underset{=}{G}^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega)$ from the divergence-free vector solutions of equation (2.13), or equivalently from

$$\nabla^2 \underset{\sim}{F}_\lambda(\underset{\sim}{r}) = \lambda \underset{\sim}{F}_\lambda(\underset{\sim}{r}) \tag{3.3}$$

It is possible (see [40]) to write the two independent divergence-free solutions of equation (3.3) in the form

$$\underset{\sim}{M}_\lambda(\underset{\sim}{r}) = \nabla \times (\underset{\sim}{a}\, \psi_\lambda) \tag{3.4}$$

$$\underset{\sim}{N}_\lambda(\underset{\sim}{r}) = \frac{1}{k}\left[\nabla \times (\nabla \times \underset{\sim}{a}\, \psi_\lambda')\right] \tag{3.5}$$

where ψ_λ, ψ_λ' satisfy equation (3.1), and k (dimensions of wavenumber) and the direction of the unit vector $\underset{\sim}{a}$ are adjusted to make the function $\underset{\sim}{F}_\lambda = \underset{\sim}{M}_\lambda + \underset{\sim}{N}_\lambda$ satisfy the same boundary conditions as the vector potential $\underset{\sim}{A}$.

The functions $\underset{\sim}{M}_\lambda(\underset{\sim}{r})$ and $\underset{\sim}{N}_\lambda(\underset{\sim}{r})$ are normalised as

$$\int \underset{\sim}{M}_\lambda^* \underset{\sim}{M}_{\lambda'}\, d^3\underset{\sim}{r} = \int \underset{\sim}{N}_\lambda^* \underset{\sim}{N}_{\lambda'}\, d^3\underset{\sim}{r} = \Lambda_\lambda\, \delta_{\lambda\lambda'} \tag{3.6}$$

We then have

$$\underset{=}{G}^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega) = \sum_\lambda \frac{1}{\Lambda_\lambda\left(\frac{\omega^2}{c^2} + \lambda\right)} \left(\underset{\sim}{M}_\lambda(\underset{\sim}{r}) \underset{\sim}{M}_\lambda^*(\underset{\sim}{r}') + \underset{\sim}{N}_\lambda(\underset{\sim}{r}) \underset{\sim}{N}_\lambda^*(\underset{\sim}{r}') \right) \tag{3.7}$$

with $\underset{\sim}{M}_\lambda \underset{\sim}{M}_\lambda^*$ and $\underset{\sim}{N}_\lambda \underset{\sim}{N}_\lambda^*$ being the diadics formed out of the vectors $\underset{\sim}{M}_\lambda$ and $\underset{\sim}{N}_\lambda$.

We now turn our attention to the problem in which the oscillators are between two parallel perfectly conducting plates, separation L [38]. Since the plates are perfectly conducting, the tangential component of the electric field and the electrostatic potential are zero there. We use a co-ordinate system in which the origin is on one of the plates and the positive z-axis is normal to the plates, directed towards the other plate. The boundary conditions are then

$$A_x = A_y = 0, \quad \frac{\partial A_z}{\partial z} = 0 \quad \text{and} \quad \phi = 0 \;, \quad z = 0, L \tag{3.8}$$

We obtain $G^{(1)}(\underset{\sim}{x}, \underset{\sim}{x}')$ using functions χ_λ as per equations (3.1) and (3.2) where

$$\chi_\lambda(\underset{\sim}{x}) = \frac{1}{\sqrt{2\pi^2 L}}\, e^{ik_1 x}\, e^{ik_2 y} \sin\frac{n\pi z}{L} \tag{3.9}$$

$$\lambda = -\left(k_1^2 + k_2^2 + \frac{n^2\pi^2}{L^2}\right) = -k_n^2$$

giving

$$G^{(1)}(\underset{\sim}{x}, \underset{\sim}{x}') = \frac{-1}{2\pi^2 L} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi z}{L}\right) \sin\left(\frac{n\pi z'}{L}\right) \times \int_{-\infty}^{\infty}\!\!\int_{-\infty}^{\infty} \frac{dk_1\, dk_2 \exp[i\{k_1(x-x') + k_2(y-y')\}]}{k_n^2} \tag{3.10}$$

For the construction of $\underset{=}{G}^{(2)}(\underset{\sim}{x}, \underset{\sim}{x}'; \omega)$ we use

$$\underset{\sim}{M}_\lambda(\underset{\sim}{x}) = \operatorname{curl}\left\{\exp[i(k_1 x + k_2 y)] \sin\left(\frac{n\pi z}{L}\right) \underset{\sim}{a}_3\right\}$$

$$= i \sin\frac{n\pi z}{L} \exp[i(k_1 x + k_2 y)] \left(k_2 \underset{\sim}{a}_1 - k_1 \underset{\sim}{a}_2\right) \tag{3.11}$$

and

$$\underset{\sim}{N}_\lambda(\underset{\sim}{x}) = \frac{1}{k_n} \operatorname{curl}\operatorname{curl}\left\{\exp[i(k_1 x + k_2 y)] \cos\left(\frac{n\pi z}{L}\right) \underset{\sim}{a}_3\right\}$$

$$= \frac{1}{k_n}\left\{ i \sin\frac{n\pi z}{L}\left[-k_1 \frac{n\pi}{L} \underset{\sim}{a}_1 - k_2 \frac{n\pi}{L} \underset{\sim}{a}_2\right] + (k_1^2 + k_2^2) \cos\frac{n\pi z}{L} \underset{\sim}{a}_3 \right\} \times \exp[i(k_1 x + k_2 y)] \tag{3.12}$$

where $\lambda = -k_n^2$

and $\underset{\sim}{a}_1, \underset{\sim}{a}_2, \underset{\sim}{a}_3$ are unit vectors in the x, y, z directions respectively.

Normalising $\underset{\sim}{M}_\lambda$ and $\underset{\sim}{N}_\lambda$ we find

$$\int \underset{\sim}{M}^*_\lambda \cdot \underset{\sim}{M}_{\lambda'} \, d^3\underset{\sim}{r} = 2\pi^2 L (k_1^2 + k_2^2) \delta(k_1 - k_1') \delta(k_2 - k_2') \delta_{nn'}$$

$$= \int \underset{\sim}{N}^*_\lambda \underset{\sim}{N}_{\lambda'} \, d^3\underset{\sim}{r} \tag{3.13}$$

Also $\underset{\sim}{E}_\lambda = \underset{\sim}{M}_\lambda + \underset{\sim}{N}_\lambda$ is seen to satisfy the boundary conditions of this problem.

Using equation (3.7) we then have

$$\underset{=}{G}^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega) = \sum_{n=0}^{\infty} \frac{1}{\epsilon_n 2\pi^2 L} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{dk_1 dk_2 \exp[i\{k_1(x-x') + k_2(y-y')\}]}{\left(\frac{\omega^2}{c^2} - k_n^2\right)\left(k_n^2 - \frac{n^2\pi^2}{L^2}\right)}$$

$$\times \Big\{ (\underset{\sim}{a}_1 k_2 - \underset{\sim}{a}_2 k_1)(\underset{\sim}{a}_1 k_2 - \underset{\sim}{a}_2 k_1) \sin\frac{n\pi z}{L} \sin\frac{n\pi z'}{L}$$

$$+ \frac{1}{k_n^2}\left(\frac{n\pi}{L}\right)^2 (\underset{\sim}{a}_1 k_1 + \underset{\sim}{a}_2 k_2)(\underset{\sim}{a}_1 k_1 + \underset{\sim}{a}_2 k_2) \sin\frac{n\pi z}{L} \sin\frac{n\pi z'}{L}$$

$$- \frac{1}{k_n^2}\left(\frac{n\pi}{L}\right)(k_1^2 + k_2^2)(\underset{\sim}{a}_1 k_1 + \underset{\sim}{a}_2 k_2)(\underset{\sim}{a}_3) \sin\frac{n\pi z}{L} \cos\frac{n\pi z'}{L}$$

$$+ \frac{1}{k_n^2}\left(\frac{n\pi}{L}\right)(k_1^2 + k_2^2)(\underset{\sim}{a}_3)(\underset{\sim}{a}_1 k_1 + \underset{\sim}{a}_2 k_2) \cos\frac{n\pi z}{L} \sin\frac{n\pi z'}{L}$$

$$+ \frac{1}{k_n^4}(k_1^2 + k_2^2)^2 \underset{\sim}{a}_3 \underset{\sim}{a}_3 \cos\frac{n\pi z}{L} \cos\frac{n\pi z'}{L} \Big\} \tag{3.14}$$

with
$$\epsilon_n = \begin{cases} 2 & n = 0 \\ 1 & n \neq 0 \end{cases}$$

where the expressions of the type $(\underset{\sim}{a}_\alpha k_\beta - \underset{\sim}{a}_\gamma k_\delta)(\underset{\sim}{a}_\tau k_\sigma)$ are the diadics formed from the vectors $(\underset{\sim}{a}_\alpha k_\beta - \underset{\sim}{a}_\gamma k_\delta)$ and $\underset{\sim}{a}_\tau k_\tau$

Substituting equations (3.10) and (3.14) into equation (2.16) we obtain after simplification

$$\underline{\underline{G}}(\underline{r},\underline{r}';\omega) = \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{bmatrix} \tag{3.15}$$

where

$$S_{\alpha\beta} = \left(\frac{\omega^2}{c^2}\delta_{\alpha\beta} - \frac{\partial^2}{\partial r_\alpha \partial r_\beta}\right) g_1(\underline{r},\underline{r}';\omega) + \frac{\omega^2}{c^2}\delta_{\alpha 3}\delta_{\beta 3}\, g_2(\underline{r},\underline{r}';\omega) \tag{3.16}$$

with

$$g_1(\underline{r},\underline{r}';\omega) = \frac{1}{2\pi^2 L}\sum_{n=1}^{\infty} \sin\frac{n\pi z}{L}\sin\frac{n\pi z'}{L}$$

$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dk_1\, dk_2\, \frac{\exp[\,i\{k_1(x-x') + k_2(y-y')\}]}{\frac{\omega^2}{c^2} - k_n^2} \tag{3.17}$$

and

$$g_2(\underline{r},\underline{r}';\omega) = \frac{1}{2\pi^2 L}\sum_{n=0}^{\infty} \cos\frac{n\pi(z+z')}{L}$$

$$\times \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dk_1\, dk_2\, \frac{\exp[\,i\{k_1(x-x') + k_2(y-y')\}]}{\epsilon_n\left(\frac{\omega^2}{c^2} - k_n^2\right)} \tag{3.18}$$

3.2 The Non-Retarded Limit [38]

For notational convenience in this problem we define a variable

$$\rho = \left\{ (x-x')^2 + (y-y')^2 \right\}^{1/2} \tag{3.19}$$

and obtain the interaction in terms of

$$\rho_{12} = \left\{ (x_1 - x_2)^2 + (y_1 - y_2)^2 \right\}^{1/2} \tag{3.20}$$

The non-retarded limit ($c \to \infty$) corresponds to the case when both L and R (and hence ρ_{12}) are much less than the chacteristic wavelength

$$\lambda_0 = 2\pi c / \omega_0 \tag{3.21}$$

Considering firstly the case where $\rho \gg L$ we note from equations (3.16) and (2.16) that as $c \to \infty, -g_1 \to G^{(1)}$ hence we start with

$$-g_1(\underline{r}, \underline{r}'; -i\xi) = \frac{1}{2\pi^2 L} \sum_{n=1}^{\infty} \sin\frac{n\pi z}{L} \sin\frac{n\pi z'}{L} \int_0^{\infty} \mathcal{K} d\mathcal{K} \int_0^{2\pi} \frac{d\theta \, e^{i\mathcal{K}\rho\cos\theta}}{\xi^2/c^2 + \mathcal{K}^2 + \frac{n^2\pi^2}{L^2}} \tag{3.22}$$

where

$$\mathcal{K} = \left(k_1^2 + k_2^2 \right)^{1/2}$$

Using the formulae

$$\int_0^{2\pi} d\theta \exp(i\mathcal{K}\rho\cos\theta) = 2\pi J_0(\mathcal{K}\rho) \tag{3.23}$$

and

$$\int_0^{\infty} \frac{\mathcal{K} d\mathcal{K} \, J_0(\mathcal{K}\rho)}{\frac{\xi^2}{c^2} + \mathcal{K}^2 + \frac{n^2\pi^2}{L^2}} = 2\pi \, K_0\left\{ \rho \left(\xi^2/c^2 + \frac{n^2\pi^2}{L^2} \right)^{1/2} \right\} \tag{3.24}$$

then substituting into equation (3.22) and letting $c \to \infty$ we get

$$G^{(1)}(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{+1}{\pi L} \sum_{n=1}^{\infty} K_0\left(\frac{n\pi\rho}{L}\right) \sin\frac{n\pi z}{L} \sin\frac{n\pi z'}{L} \tag{3.25}$$

Now we also have that

$$Tr\{[\nabla_R \nabla_{R'} \underset{\sim}{G}^{(1)}(\underset{\sim}{r}, \underset{\sim}{r}')] . [\nabla_{r'} \nabla_r G^{(1)}(\underset{\sim}{r}', \underset{\sim}{r})] = \sum_{i=1}^{3} \sum_{j=1}^{3} \left[\frac{\partial^2 G^{(1)}}{\partial x_i \partial x_j}\right]^2 \tag{3.26}$$

For large ρ/L , we need retain only the first term in equation (3.25) and using the asymptotic form for $K_0(\pi\rho/L)$, on substituting into equations (3.26) and (2.23) we obtain

$$E(R) \simeq \frac{-2\pi^5 \hbar e^4}{m^2 \omega_0^3 L^6} \left(\frac{\exp(-2\pi\rho_{12}/L)}{2\pi \rho_{12}/L} \right) \cos^2\left(\frac{\pi(z_1+z_2)}{L}\right) \tag{3.27}$$

When L is large, in equation (3.22) we sum over using Poisson's Summation Formula [41] before integrating over χ and θ to get

$$-g_1(\underset{\sim}{r}, \underset{\sim}{r}'; -i\zeta) = \frac{1}{2\pi} \int_0^{\infty} \frac{\chi d\chi J_0(\chi\rho)}{K\{\exp(2KL)-1\}} \times \Big[\exp(K|z-z'|) + \exp(-K|z-z'|+2KL) - \exp(K|z+z'|) - \exp(-K|z+z'| + 2KL) \Big] \tag{3.28}$$

where $K = (\chi^2 + \zeta^2/c^2)^{1/2}$

Re-arranging equation (3.28) and using the identity

$$\int_0^{\infty} \frac{\chi d\chi\, J_0(\chi\rho)}{\{\chi^2 + \zeta^2/c^2\}^{1/2}} \exp[-|z-z'|\{\chi^2+\zeta^2/c^2\}^{1/2}] = \frac{\exp\{-\zeta R/c\}}{R} \tag{3.29}$$

where $R = \{(z-z')^2 + \rho^2\}^{1/2}$ we then have

$$-g_1(\underline{r},\underline{r}';-i\xi) = \frac{1}{4\pi}\left[\frac{\exp(-\xi R/c)}{R} + 2\int_0^\infty \frac{\kappa\, d\kappa\, J_0(\kappa\rho)}{K\{\exp(2KL)-1\}}\right.$$

$$\left.\times\Big\{\cosh\{K(z-z')\} - \cosh\{K(z+z'-L)\}\exp(KL)\Big\}\right] \tag{3.30}$$

In this form the Green function shows explicitly the free space term plus correction terms due to the boundaries.

Using now the non-retarded form of equation (3.30) and substituting $2\kappa L = t$ we obtain

$$G^{(1)}(\underline{r},\underline{r}') = \frac{1}{4\pi}\left[\frac{1}{R} + \frac{1}{L}\int_0^\infty \frac{dt\, J_0(\rho t/2L)}{\exp(t)-1}\right.$$

$$\left.\times\left\{\cosh\left(\frac{(z-z')t}{2L}\right) - \cosh\left(\frac{(z+z'-L)t}{2L}\right)\exp\frac{t}{2}\right\}\right] \tag{3.31}$$

Now, since the main contribution to the integral comes from the neighbourhood of $t \to 0$ we expand the Bessel and cosh functions in power series and integrate term by term to give

$$G^{(1)}(\underline{r},\underline{r}') = \frac{1}{4\pi}\left[\frac{1}{R} + \frac{2}{L}\left\{-\ln 2 + \left(\frac{(z-z')^2}{8L^2} - \frac{\rho^2}{16L^2}\right)\zeta(3)\right.\right.$$

$$\left.\left. - \left(\frac{(z+z'-L)^2}{8L^2} - \frac{\rho^2}{16L^2}\right)\zeta(3,\tfrac{1}{2}) + O\left(\frac{(z-z')^4}{L}\right)\right\}\right]$$

$$= \frac{1}{4\pi}\left[\frac{1}{R} - \frac{2\ln 2}{L} + \frac{\zeta(3)}{4L^3}\left\{3\rho^2 - 7(z+z'-L)^2 + (z-z')^2\right\} + \cdots\right] \tag{3.32}$$

In equation (3.32) $\zeta(3,\frac{1}{2})$ is a generalised zeta function satisfying $\zeta(s,\frac{1}{2}) = \zeta(s)(2^s - 1)$ [42]. For the case when $(z_1 + z_2 - L) << L$ we substitute into equations (3.26) and

(3.23) neglecting the term $(z+z'-L)^2/L^3$. Hence when the oscillators are nearly in the middle of the two conducting planes (i.e. $(z_1+z_2-L) << L$) we have

$$E(R) \approx E_L(R)\left\{1 + \frac{5}{6}\zeta(3)\left(\frac{R}{L}\right)^3\left(\frac{3(z_1-z_2)^2}{R^2} - 1\right)\right\} \qquad (3.33)$$

where $E_L(R) = -3\hbar e^4/4m^2\omega_0^3 R^6$ is the non-retarded London interaction between oscillators in free space.

For the case when $(z_1+z_2) << L$, the oscillators close to one of the conducting planes, we rearrange (3.28) into the form

$$G^{(1)}(x,x') = \frac{1}{4\pi}\left[\frac{1}{R} - \frac{1}{R_+} + \frac{1}{L}\int_0^\infty \frac{dt\, J_0(\rho t/2L)}{\exp(t)-1}\right.$$
$$\left. \times\left\{\cosh\left(\frac{(z-z')t}{2L}\right) - \cosh\left(\frac{(z+z')t}{2L}\right)\right\}\right] \qquad (3.34)$$

where $R_+ = \{(z+z')^2+\rho^2\}^{1/2}$

and proceed as before to obtain

$$E(R) = E_L(R)\left\{\frac{2}{3}\left(1 - \zeta(3)\frac{\rho_{12}^3}{L^3}\right)\right\} \qquad (3.35)$$

When $(z_1+z_2) \sim L$, the oscillators one near each conducting plane, we start with

$$G^{(1)}(x,x') = \frac{1}{4\pi L}\int_0^\infty \frac{dt\, J_0(\rho t/2L)}{\exp(t)-1}\exp\left(\frac{t}{2}\right)\left\{\cosh\left\{\frac{(|z-z'|-L)t}{2}\right\} - \cosh\left\{\frac{(|z+z'|-L)t}{2}\right\}\right\} \qquad (3.36)$$

to obtain

$$E(R) \approx E_L(R)\left\{\left(\frac{R}{L}\right)^6\frac{\left[\frac{7}{8}\zeta(3)\right]^2}{6} + \cdots\right\} \qquad (3.37)$$

the neglected terms being $O(\rho_{12}/L)^2$ and $O\{(|z_1 \pm z_2|-L)/L\}^2$.

We note at this stage that equation (3.33) implies an enhancement from the free space value when $|z_1 - z_2| > \rho_{12}/\sqrt{2}$ but a diminishing when $z_1 = z_2$, i.e. the oscillators on the medial plane.

3.3 The Retarded region [38]

In the retarded region it is necessary to use the Green function of equation (3.15).

For $\rho \gg L$ we start with (see equations (3.22) - (3.24))

$$g_1(\underline{x},\underline{x}';-i\xi) = \frac{-1}{\pi L}\sum_{n=1}^{\infty} \sin\frac{n\pi z}{L}\sin\frac{n\pi z'}{L} K_0\left[\rho\left\{\frac{\xi^2}{c^2}+\left(\frac{n\pi}{L}\right)^2\right\}^{1/2}\right] \qquad (3.38)$$

and

$$g_2(\underline{x},\underline{x}';-i\xi) = \frac{-1}{\pi L}\sum_{n=0}^{\infty} \frac{1}{\epsilon_n}\cos\frac{n\pi(z+z')}{L} K_0\left[\rho\left\{\frac{\xi^2}{c^2}+\left(\frac{n\pi}{L}\right)^2\right\}^{1/2}\right] \qquad (3.39)$$

Substitution now into equations (3.15) and (2.22) yields, after some straightforward algebra

$$E(R) \simeq -\frac{192}{\pi}\frac{\hbar c e^4}{m^2\omega_0^4}\frac{1}{L^2\rho_{12}^5} \qquad (3.40)$$

which represents an enhancement from the Casimir-Poldor free space result [11].

For the case when $R \ll L$ we begin with equation (3.38) rewritten with

$$\sin\frac{n\pi z}{L}\sin\frac{n\pi z'}{L} = \frac{1}{2}\left\{\cos\left(\frac{n\pi}{L}(z-z')\right)-\cos\left(\frac{n\pi}{L}(z+z')\right)\right\}$$

and apply Poisson's Summation Formula [41] to obtain

$$-g_1(\underline{x},\underline{x}';-i\xi) = \frac{1}{4\pi}\sum_{l=-\infty}^{\infty}\left(\frac{\exp(-R_l\xi/c)}{R_l}-\frac{\exp(-R_l'\xi/c)}{R_l'}\right) \qquad (3.41)$$

where $R_l^2 = (2lL+|z-z'|)^2+\rho^2$ and $R_l'^2 = (2lL+|z+z'|)^2+\rho^2$.

We now use the formula

$$\frac{\exp\{-\eta(t^2+s^2-2ts\cos\theta)^{1/2}\}}{(t^2+s^2-2ts\cos\theta)^{1/2}} = \sum_{l'=0}^{\infty}\frac{(2l'+1)}{\sqrt{ts}}K_{l'+\frac{1}{2}}(t\eta)\,I_{l'+\frac{1}{2}}(s\eta)\,P_{l'}(\cos\theta) \qquad (3.42)$$

$$t > s$$

to write

$$\sum_{l=-\infty}^{\infty} \frac{\exp(-R_l \zeta/c)}{R_l} = \frac{\exp(-\zeta R/c)}{R} + 2\sum_{l'=0}^{\infty}(4l'+1)\sum_{l=1}^{\infty}\frac{1}{\sqrt{2lLR}}$$

$$\times K_{2l'+\frac{1}{2}}(2lL\zeta/c)\, I_{2l'+\frac{1}{2}}(\zeta R/c)\, P_{2l'}\left(\frac{|z-z'|}{R}\right)$$

(3.43)

This expansion is permissible since $2lL \gg R$, $l \neq 0$

For the second sum over $\exp(-\zeta R_l'/c)/R_l'$ we write

$$z+z' = 2L\beta - \delta \qquad 0<\beta<1 \qquad \delta = O(\tfrac{1}{L})$$

We then have

$$R_l'^{\,2} = \{2L(l+\beta)\}^2 + 2L(l+\beta)R''\left(\frac{z+z'-2l\beta}{R''}\right) + (R'')^2 \tag{3.44}$$

where $(R'')^2 = (z+z'-2l\beta)^2 + \rho^2$. Now $R'' \ll 2L(l+\beta)$

so using equation (3.42) we have

$$\sum_{l=-\infty}^{\infty} \frac{\exp(-R_l' \zeta/c)}{R_l'} = \sum_{l'=0}^{\infty}(2l+1)\sum_{l=1}^{\infty}\left\{\frac{K_{l'+\frac{1}{2}}\{2L\zeta(l-\beta)/c\}}{\{2L(l-\beta)\}^{\frac{1}{2}}} + (-1)^{l'}\frac{K_{l'+\frac{1}{2}}\{2L\zeta(l+\beta-1)/c\}}{\{2L(l+\beta-1)\}^{\frac{1}{2}}}\right\}$$

$$\times \frac{I_{l'+\frac{1}{2}}(\zeta R''/c)}{\sqrt{R''}}\, P_{l'}\left(\frac{(z+z')-2L\beta}{R''}\right)$$

(3.45)

Combining now equations (3.43) and (3.45) we have

$$g_1(\underline{r}, \underline{r}'; -i\zeta) = g_1^{(0)} + g_1^{(1)}; \quad g_1^{(0)} = \frac{-\exp(\zeta R/c)}{4\pi R} \tag{3.46}$$

where $g_1^{(1)}$ is the correction to the free-space Green function.

After substitution of equation (3.46) into equation (3.15) we carry out the integration over ζ in equation (2.22) by expanding the Bessel functions $J_{l+\frac{1}{2}}(R\zeta/c)$, $J_{l+\frac{1}{2}}(R''\zeta/c)$ in powers of their arguments, retaining terms of order $\left\{(\zeta R/2c)^{5/2}/\sqrt{R}\right\}$ and $\left\{(\zeta R''/c.2)^{5/2}/\sqrt{R''}\right\}$. Two limiting cases then become apparent.

For $R\omega_0/c \ll 1$ and $L \ll \lambda_0$ we have

$$E(R) \approx E_L(R)\left[1 + \left(\frac{3(z_1-z_2)^2}{R^2} - 1\right)\frac{2}{3\pi}\left(\frac{c}{\omega_0 L}\right)\left\{\left(\frac{R}{L}\right)^3 \zeta(4) + O\left(\frac{R}{L}\right)^5\right\}\cdots\right] \tag{3.47}$$

For $R\omega_0/c \gg 1$ and $L \gg \lambda_0$ we have

$$E(R) \approx E_{CP}(R)\left[1 + \left(\frac{3(z_1-z_2)^2}{R^2} - 1\right)\frac{2}{69}\left(\frac{R}{L}\right)^4 \zeta(4) + O\left(\frac{R}{L}\right)^6\right] \tag{3.48}$$

Here

$$E_{CP}(R) = \frac{-23\hbar c\, e^4}{4\pi R^7 m^2 \omega_0^4} \tag{3.49}$$

is the Casimir- Polder result for the retarded interaction in free space [11].

We note that as was the case in equation (3.33) the interaction is enhanced for $|z_1 - z_2| > (\rho_{12}/\sqrt{2})$.

CHAPTER 4

4.1 The Green Functions

We now turn our attention to the consideration of the oscillators when they are inside an infinitely long rectangular duct, sides of length a and b, with perfectly conducting sides.

We use a co-ordinate system in which the origin is at one corner of the duct with the positive x and y axes lying in the walls of the duct with the z axis directed along the duct, parallel to the walls. Our boundary conditions are then

$$\phi = 0 \quad x = 0, a \qquad \phi = 0 \quad y = 0, b$$

$$A_x = A_z = \frac{\partial A_y}{\partial y} = 0 \quad y = 0, b \qquad A_y = A_z = \frac{\partial A_x}{\partial x} = 0 \quad x = 0, a \tag{4.1}$$

We proceed as in Chapter 3 to construct the Green function for this configuration obtaining

$$G^{(1)}(\underset{\sim}{x}, \underset{\sim}{x}') = \frac{-2}{\pi a b} \sum_{n=1}^{\infty} \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a}$$

$$\times \sum_{m=1}^{\infty} \sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \int_{-\infty}^{\infty} \frac{dk \exp[ik(z-z')]}{k_{mn}^2} \tag{4.2}$$

where $k_{mn}^2 = k^2 + \frac{m^2\pi^2}{b^2} + \frac{n^2\pi^2}{a^2}$

For the construction of the Green diadic we use

$$\underset{\sim}{M}_\lambda(\underset{\sim}{x}) = \nabla \times \left(\underset{\sim}{a}_3 \cos\frac{n\pi x}{a} \cos\frac{m\pi y}{b} e^{ikz} \right)$$

$$= -\frac{m\pi}{b} \cos\frac{n\pi x}{a} \sin\frac{m\pi y}{b} e^{ikz} \underset{\sim}{a}_1 + \frac{n\pi}{a} \sin\frac{n\pi x}{a} \cos\frac{m\pi y}{b} e^{ikz} \underset{\sim}{a}_2 \tag{4.3}$$

$$\underset{\sim}{N}_\lambda(\underset{\sim}{r}) = \frac{1}{k_{mn}} \nabla \times \left(\nabla \times \underset{\sim}{a}_3 \sin\frac{n\pi x}{a} \sin\frac{m\pi y}{b} e^{ikz}\right)$$

$$= \frac{e^{ikz}}{k_{mn}} \left(ik\frac{n\pi}{a}\cos\frac{n\pi x}{a}\sin\frac{m\pi y}{b}\underset{\sim}{a}_1 + ik\frac{m\pi}{b}\sin\frac{n\pi x}{a}\cos\frac{m\pi y}{b}\underset{\sim}{a}_2 \right.$$

$$\left. + (k_{mn}^2 - k^2)\sin\frac{n\pi x}{a}\sin\frac{m\pi y}{b}\underset{\sim}{a}_3 \right) \qquad (4.4)$$

with $\lambda = -k_{mn}^2$

The $\underset{\sim}{M}_\lambda$ and $\underset{\sim}{N}_\lambda$ are normalised according to

$$\int \underset{\sim}{M}^*_\lambda \cdot \underset{\sim}{M}_{\lambda'} \, d^3\underset{\sim}{r} = \int \underset{\sim}{N}^*_\lambda \cdot \underset{\sim}{N}_{\lambda'} \, d^3\underset{\sim}{r}$$

$$= \frac{\pi ab}{2}(k_{mn}^2 - k^2)\delta(k-k')\delta_{mm'}\delta_{nn'} \qquad (4.5)$$

We therefore have

$$\Lambda_\lambda = \frac{ab\pi}{2}(k_{mn}^2 - k^2) \qquad (4.6)$$

and hence

$$\underset{=}{G}^{(2)}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega) = \frac{2}{ab\pi} {\sum_{n=0}^{\infty}}' {\sum_{m=0}^{\infty}}' \int_{-\infty}^{\infty} \frac{dk \, e^{ik(z-z')}}{(k_{mn}^2 - k^2)(\frac{\omega^2}{c^2} - k_{mn}^2)}$$

$$\times \left\{ \underset{\sim}{a}_1\underset{\sim}{a}_1 \cos\frac{n\pi x}{a}\cos\frac{n\pi x'}{a}\sin\frac{m\pi y}{b}\sin\frac{m\pi y'}{b}\left(\frac{\pi^2 m^2}{b^2} + \frac{k^2}{k_{mn}^2}\frac{\pi^2 n^2}{a^2}\right) \right.$$

$$+ \underset{\sim}{a}_2\underset{\sim}{a}_2 \sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}\cos\frac{m\pi y}{b}\cos\frac{m\pi y'}{b}\left(\frac{\pi^2 n^2}{a^2} + \frac{k^2}{k_{mn}^2}\frac{\pi^2 m^2}{b^2}\right)$$

$$+ \underset{\sim}{a}_3\underset{\sim}{a}_3 \sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}\sin\frac{m\pi y}{b}\sin\frac{m\pi y'}{b}(k_{mn}^2 - k^2)^2 / k_{mn}^2$$

$$+ \underset{\sim}{a}_1 \underset{\sim}{a}_2 \cos\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \sin\frac{m\pi y}{b} \cos\frac{m\pi y'}{b} \left(\frac{\pi^2 k^2 mn}{ab\, k_{mn}^2} - \frac{\pi^2 mn}{ab}\right)$$

$$+ \underset{\sim}{a}_2 \underset{\sim}{a}_1 \sin\frac{n\pi x}{a} \cos\frac{n\pi x'}{a} \cos\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \left(\frac{\pi^2 k^2 mn}{ab\, k_{mn}^2} - \frac{\pi^2 mn}{ab}\right)$$

$$+$$

$$+ \underset{\sim}{a}_1 \underset{\sim}{a}_3 \cos\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \left(\frac{k_{mn}^2 - k^2}{k_{mn}^2}\right) \frac{\pi i k n}{a}$$

$$- \underset{\sim}{a}_3 \underset{\sim}{a}_1 \sin\frac{n\pi x}{a} \cos\frac{n\pi x'}{a} \sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \left(\frac{k_{mn}^2 - k^2}{k_{mn}^2}\right) \frac{\pi i k n}{a}$$

$$+ \underset{\sim}{a}_2 \underset{\sim}{a}_3 \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \cos\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \left(\frac{k_{mn}^2 - k^2}{k_{mn}^2}\right) \frac{\pi i k m}{b}$$

$$- \underset{\sim}{a}_2 \underset{\sim}{a}_3 \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \left(\frac{k_{mn}^2 - k^2}{k_{mn}^2}\right) \frac{\pi i k m}{b} \Bigg\} \quad (4.7)$$

where the prime on the summation denotes that the zero term is to be taken with weight ½.

Combining now equations (4.2) and (4.7) according to equation (2.16) we obtain

$$\underset{=}{G}(\underset{\sim}{r}, \underset{\sim}{r}'; \omega) = \begin{bmatrix} S_{11} & S_{12} & S_{13} \\ S_{21} & S_{22} & S_{23} \\ S_{31} & S_{32} & S_{33} \end{bmatrix} \quad (4.8)$$

where
$$S_{\alpha\beta} = \left(\frac{\omega^2}{c^2}\delta_{\alpha\beta} - \frac{\partial^2}{\partial r_\alpha \partial r'_\beta}\right) \hat{g}_1(\underset{\sim}{r}, \underset{\sim}{r}'; \omega)$$
$$+ \frac{\omega^2}{c^2}\delta_{\alpha 1}\delta_{\beta 1}\, \hat{g}_2(\underset{\sim}{r}, \underset{\sim}{r}'; \omega)$$
$$+ \frac{\omega^2}{c^2}\delta_{\alpha 2}\delta_{\beta 2}\, \hat{g}_3(\underset{\sim}{r}, \underset{\sim}{r}'; \omega) \quad (4.9)$$

with
$$\hat{g}_1(\underset{\sim}{r}, \underset{\sim}{r}'; \omega) = \frac{2}{\pi ab} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b}$$
$$\times \int_{-\infty}^{\infty} \frac{dk\, e^{ik(z-z')}}{\frac{\omega^2}{c^2} - k_{mn}^2} \quad (4.10)$$

$$\hat{g}_2(\underset{\sim}{r},\underset{\sim}{r}';\omega) = \frac{2}{\pi ab}\sum_{n=0}^{\infty}{}'\sum_{m=1}^{\infty} \cos\frac{n\pi(x+x')}{a}\sin\frac{m\pi y}{b}\sin\frac{m\pi y'}{b}$$

$$\times \int_{-\infty}^{\infty} dk\, \frac{e^{ik(z-z')}}{\frac{\omega^2}{c^2} - k_{mn}^2} \qquad (4.11)$$

and
$$\hat{g}_3(\underset{\sim}{r},\underset{\sim}{r}';\omega) = \frac{2}{\pi ab}\sum_{n=1}^{\infty}\sum_{m=0}^{\infty}{}' \sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}\cos\frac{m\pi}{b}(y+y')$$

$$\times \int_{-\infty}^{\infty} dk\, \frac{e^{ik(z-z')}}{\frac{\omega^2}{c^2} - k_{mn}^2} \qquad (4.12)$$

4.2 The Non-retarded Limit

We consider firstly the non-retarded case where the dimensions of the duct, a and b, and R are both much less than the characteristic wavelength of the system $\lambda_0 = 2\pi c/\omega_0$

Considering the case when $|z - z'| >> a, b$ (hence $R >> a, b$) we start with

$$- g_1(\underline{x}, \underline{x}'; -i\xi) = \frac{2}{\pi ab} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \int_{-\infty}^{\infty} \frac{dk\, e^{ik(z-z')}}{k_{nm}^2 + \xi^2/c^2}$$

$$= \frac{2}{\pi ab} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \int_{-\infty}^{\infty} \frac{dk\, e^{ik(z-z')}}{\beta_{nm}^2 + k^2}$$

(4.13)

where $$\beta_{nm}^2 = \xi^2/c^2 + \frac{n^2\pi^2}{a^2} + \frac{m^2\pi^2}{b^2}$$

Evaluating the integral according to

$$\int_{-\infty}^{\infty} \frac{e^{ik(z-z')}}{\beta_{nm}^2 + k^2} dk = \frac{\pi}{\beta_{nm}} e^{-\beta_{nm}|z-z'|} \qquad (4.14)$$

and retaining only the first term of the double sum since $|z-z'| >> a, b$ we have

$$-g_1(\underline{x}, \underline{x}'; -i\xi) = \frac{2}{ab\beta_{11}} \sin\frac{\pi x}{a} \sin\frac{\pi x'}{a} \sin\frac{\pi y}{b} \sin\frac{\pi y'}{b} \exp[-\beta_{11}|z-z'|]$$

(4.15)

Now for the non-retarded case, $c \to \infty$ we then have

$$G^{(1)}(\underline{x}, \underline{x}') = \frac{2}{\pi(a^2+b^2)^{1/2}} \sin\frac{\pi x}{a} \sin\frac{\pi x'}{a} \sin\frac{\pi y}{b} \sin\frac{\pi y'}{b}$$

$$\times \exp\left[\frac{-\pi(a^2+b^2)^{1/2}|z-z'|}{ab}\right] \qquad (4.16)$$

Using now equations (3.26) and (2.23) we then have

$$E(R) \simeq \frac{-8\pi^4 \hbar e^4}{m^2 \omega_0^3 (a^2+b^2)} \exp\left[-2\pi (a^2+b^2)^{1/2} |z-z'| / ab\right]$$

$$\times \left\{ \frac{\sin^2\left(\frac{\pi y}{b}\right) \sin^2\left(\frac{\pi y'}{b}\right)}{a^4} + \frac{\sin^2\left(\frac{\pi x}{a}\right) \sin^2\left(\frac{\pi x'}{a}\right)}{b^4} \right.$$

$$\left. + \frac{\sin^2\left(\frac{\pi x}{a}\right) \sin^2\left(\frac{\pi y'}{b}\right) + \sin^2\left(\frac{\pi x'}{a}\right) \sin^2\left(\frac{\pi y}{b}\right)}{a^2 b^2} \right\} \tag{4.17}$$

For the case when a is large, we begin by using Poisson's Summation Formula [41] in the form (for F(n) even)

$$\sum_{n=-\infty}^{\infty} F(n) = \int_{-\infty}^{\infty} F(n)\, dn + 2 \sum_{r=1}^{\infty} \int_{-\infty}^{\infty} F(n) \cos(2\pi r n)\, dn \tag{4.18}$$

Applying equation (4.18) to equation (4.10) in non-retarded form yields

$$-\hat{g}_1(\underset{\sim}{r}, \underset{\sim}{r}'; -i\zeta) = \frac{1}{2\pi^2 a} \sum_{n=1}^{\infty} \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \iint_{-\infty}^{\infty} \frac{dk\, dk_1 \exp\left[i\{k_1(y-y') + k(z-z')\}\right]}{k_1^2 + k^2 + \frac{n^2\pi^2}{a^2}}$$

$$- \frac{1}{2\pi^2 a} \sum_{n=1}^{\infty} \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \iint_{-\infty}^{\infty} \frac{dk_1\, dk \exp\left[i\{k_1(y+y') + k(z-z')\}\right]}{k_1^2 + k^2 + \frac{n^2\pi^2}{a^2}}$$

$$+ \frac{4}{\pi a b} \sum_{n=1}^{\infty} \sin\frac{n\pi x}{a} \sin\frac{n\pi x'}{a} \int_{-\infty}^{\infty} dk\, e^{ik(z-z')}$$

$$\times \sum_{r=1}^{\infty} \int_{-\infty}^{\infty} \frac{\sin\frac{m\pi y}{b} \sin\frac{m\pi y'}{b} \cos(2\pi r m)\, dm}{k^2 + \frac{m^2\pi^2}{b^2} + \frac{n^2\pi^2}{a^2}} \tag{4.19}$$

In this form $\hat{g}_1$ is seen to be composed of three parts, one being the same as obtained in section 3.2, due to the plates at x = o,a, the second being due to the plate at y = o and the third being the contribution from the plate at y = b.

If we now carry out the integration over m, we obtain for the sum over r

$$\sum_{r=1}^{\infty}\int_{-\infty}^{\infty}\frac{\sin\frac{m\pi y}{b}\sin\frac{m\pi y'}{b}\cos(2\pi r m)\,dm}{k^2+\frac{m^2\pi^2}{b^2}+\frac{n^2\pi^2}{a^2}}$$

$$=\sum_{r=1}^{\infty}\frac{b}{2}\,\frac{\exp\left[-\left(\frac{n^2\pi^2}{a^2}+k^2\right)^{1/2}.2br\right]}{\left(\frac{n^2\pi^2}{a^2}+k^2\right)^{1/2}}\Big[\cosh\left\{\left(k^2+\frac{n^2\pi^2}{a^2}\right)^{1/2}(y-y')\right\}$$

$$-\cosh\left\{\left(k^2+\frac{n^2\pi^2}{a^2}\right)^{1/2}(y+y')\right\}\Big] \qquad (4.20)$$

This is valid since $2br > (y-y')$ and $2br > y+y'$ for $r \neq 0$

When b is large, we retain only the first term in the sum over r to obtain

$$-\hat{g}_1(\mathbf{r},\mathbf{r}';-i\xi) = -\hat{g}_1^{\circ} - \frac{1}{2\pi^2 a}\sum_{n=1}^{\infty}\sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}$$

$$\times\iint_{-\infty}^{\infty}\frac{dk_1\,dk_2\exp\left[i\{k_1(y+y')+k_2(z-z')\}\right]}{k_1^2+k_2^2+\frac{n^2\pi^2}{a^2}}$$

$$+\frac{2}{\pi a}\sum_{n=1}^{\infty}\sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}\int_{-\infty}^{\infty}e^{ik(z-z')}\,dk$$

$$\times\frac{\exp\left[-\left(\frac{n^2\pi^2}{a^2}+k^2\right)^{1/2}2b\right]}{\left(\frac{n^2\pi^2}{a^2}+k^2\right)^{1/2}}\left[\cosh\left\{\left(k^2+\frac{n^2\pi^2}{a^2}\right)^{1/2}(y-y')\right\}-\cosh\left\{\left(k^2+\frac{n^2\pi^2}{a^2}\right)^{1/2}(y+y')\right\}\right]$$

(4.21)

where $\hat{g}_i^{\circ}$ is the two plate function for the plates $x = o, a$.

We now integrate over k before applying Poisson's Summation formula again to the third term, treating the second term as outlined in section 3.2 we obtain for leading terms

$$-\hat{g}_1(\underset{\sim}{r}, \underset{\sim}{r}'; -i\zeta) = -\hat{g}_i^{\circ} + \frac{1}{4\pi}\left[\frac{1}{R_b} - \frac{1}{R_{b+}} - \frac{1}{R_{y+}}\right] \tag{4.22}$$

where

$$R_b^2 = (x-x')^2 + (2b-(y-y'))^2 + (z-z')^2$$

$$R_{b+}^2 = (x-x')^2 + (2b-(y+y'))^2 + (z-z')^2$$

$$R_{y+}^2 = (x-x')^2 + (y+y')^2 + (z-z')^2$$

Use of equation (4.22) then gives us the energy as

$$E(R) = E_{2P}(R) + E_c(R) \tag{4.23}$$

where $E_{2P}(R)$ is the two plate case result of section 3.2 and $E_c(R)$ the correction due to the second pair of walls where

$$E_c(R) = E_L(R)\left\{\frac{R}{6}\left[\frac{9(\rho_{12}^4 + (y_1-y_2)^2(2b-(y_1-y_2))^2)}{R_b^5} - \frac{3(\rho_{12}^4 - (y_1-y_2)^2(2b-(y_1+y_2))^2)}{R_{b+}^5} - \frac{3(\rho_{12}^4 - (y_1-y_2)^2(y_1+y_2)^2)}{R_+^5}\right]\right.$$

$$\left. + \frac{R^3}{6}\left(\frac{1}{R_{b+}^3} + \frac{1}{R_{y+}^3} - \frac{3}{R_b^3}\right) + \right\} \tag{4.24}$$

When b is small, we sum the geometric series involved in equation (4.20) to obtain

$$-\hat{g}_1(\underset{\sim}{x},\underset{\sim}{x}';-i\zeta) = -\hat{g}_1^0 - \frac{1}{2\pi^2 a}\sum_{n=1}^{\infty} \sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}$$

$$\times \iint_{-\infty}^{\infty} \frac{dk\,dk_1 \exp[i\{k_1(y+y')+k(z-z')\}]}{k_1^2+k^2+\frac{n^2\pi^2}{a^2}}$$

$$+\frac{2}{\pi a}\sum_{n=1}^{\infty}\sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}\int_{-\infty}^{\infty} e^{ik(z-z')} dk \frac{\exp[-(\frac{n^2\pi^2}{a^2}+k^2)^{1/2}2b]}{(k^2+\frac{n^2\pi^2}{a^2})^{1/2}}$$

$$\times \frac{[\cosh\{(\frac{n^2\pi^2}{a^2}+k^2)^{1/2}(y-y')\} - \cosh\{(\frac{n^2\pi^2}{a^2}+k^2)^{1/2}(y+y')\}]}{1-\exp[-(\frac{n^2\pi^2}{a^2}+k^2)^{1/2}2b]}$$

(4.25)

Expanding the third term in equation (4.25) in a power series since b is small and retaining terms of order 2b we obtain

$$-\hat{g}_1(\underset{\sim}{x},\underset{\sim}{x}';-i\zeta) = -\hat{g}_1^0 - \frac{1}{\pi a}\sum_{n=1}^{\infty}\sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a} K_0\left[\frac{n\pi}{a}\left((z-z')^2+(y+y')^2\right)^{1/2}\right]$$

$$+\frac{1}{\pi a b}\sum_{n=1}^{\infty}\sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}\left[\frac{a}{2n}e^{-\frac{n\pi}{a}|z-z'|} - (y-y')K_0\left(\frac{n\pi}{a}(z-z')\right)\right]$$

(4.26)

For $|z-z'|/a$ large we retain the first term in each sum to obtain

$$-\hat{g}_1(\underset{\sim}{x},\underset{\sim}{x}';-i\zeta) = -\hat{g}_1^0 - \frac{1}{\pi a}\sin\frac{\pi x}{a}\sin\frac{\pi x'}{a}K_0\left[\frac{\pi}{a}\left((z-z')^2+(y+y')^2\right)^{1/2}\right]$$

$$+\frac{1}{\pi b a}\sin\frac{\pi x}{a}\sin\frac{\pi x'}{a}\left\{\frac{a}{2}e^{-\frac{\pi}{a}|z-z'|} - (y-y_0)K_0\left(\frac{\pi}{a}(z-z')\right)\right\}$$

(4.27)

Expanding the Bessel function for large values of the argument and substituting into equations (3.26) and (2.23) we obtain as before

$$E(R) = E_{2P}(R) + E_c(R)$$

where here

$$E_c(R) = \frac{-2\pi^5 \hbar e^4}{m^2 \omega_0^3 a^6} \left[\frac{\exp\left[-2\pi\left((z_1-z_2)^2+(y_1+y_2)^2\right)^{1/2}/a\right]}{2\pi\left((z_1-z_2)^2+(y_1+y_2)^2\right)^{1/2}/a} \right] \cos^2\frac{\pi(x+x')}{a}$$

$$-\frac{\hbar e^4}{2m^2\omega_0^3 a^4} \exp\left(-\frac{2\pi}{a}|z_1-z_2|\right)$$

$$-\frac{2\hbar e^4}{m^2\omega_0^3 a^2 b^2} \frac{e^{-\frac{2\pi}{a}|z_1-z_2|}}{|z_1-z_2|} \left\{ (y_1-y_2)^2 \frac{\pi^4}{a^4}\left(\sin^2\left(\frac{\pi x}{a}\right)\sin^2\left(\frac{\pi x'}{a}\right) + \cos^2\left(\frac{\pi x}{a}\right)\cos^2\left(\frac{\pi x'}{a}\right)\right) \right.$$

$$\left. + \frac{\pi^2}{a^2}\left(\cos^2\left(\frac{\pi x}{a}\right)\sin^2\left(\frac{\pi x'}{a}\right) + \sin^2\left(\frac{\pi x}{a}\right)\cos^2\left(\frac{\pi x'}{a}\right)\right) \right\} \tag{4.28}$$

4.3 Interaction in the retarded region

For the retarded interaction it is necessary to use the full Green function of equation (4.8). When a, b $\gg R$ we start with $\hat{g}_1$ in the form (see equations (4.13) and (4.14)

$$-\hat{g}_1(\underline{r},\underline{r}';-i\zeta) = \frac{2}{\pi ab}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\sin\frac{n\pi x}{a}\sin\frac{n\pi x'}{a}\sin\frac{m\pi y}{b}\sin\frac{m\pi y'}{b}$$

$$\times\frac{1}{\beta_{nm}}\exp\left[-\beta_{nm}|z-z'|\right] \qquad (4.28)$$

with $\beta_{nm}^2 = \frac{\zeta^2}{c^2} + \frac{n^2\pi^2}{a^2} + \frac{m^2\pi^2}{b^2}$, with similar expressions for $\hat{g}_2$ and $\hat{g}_3$.

We now apply Poisson's Summation formula [41] four times to equation (4.28) to give

$$-\hat{g}_1(\underline{r},\underline{r}';-i\zeta) = \frac{1}{4\pi}\sum_{r=-\infty}^{\infty}\sum_{s=-\infty}^{\infty}\left[\frac{\exp(-\zeta/c\,R_{rs})}{R_{rs}} + \frac{\exp[-\frac{\zeta}{c}R_{+rs+}]}{R_{+rs+}}\right.$$

$$\left.-\frac{\exp[-\zeta/c\,R_{+rs}]}{R_{+rs}} - \frac{\exp[-\zeta/c\,R_{rs+}]}{R_{rs+}}\right] \qquad (4.29)$$

where

$$R_{rs}^2 = [(x-x')+2ra]^2 + [(y-y')+2sb]^2 + (z-z')^2$$

$$R_{+rs+}^2 = [(x+x')+2ra]^2 + [(y+y')+2sb]^2 + (z-z')^2$$

$$R_{+rs}^2 = [(x+x')+2ra]^2 + [(y-y')+2bs]^2 + (z-z')^2$$

$$R_{rs+} = [(x-x')+2ra]^2 + [(y+y')+2sb]^2 + (z-z')^2$$

Rewriting equation (4.29) we then have

$$-\hat{g}(\underset{\sim}{r},\underset{\sim}{r}',-i\xi) = \frac{1}{4\pi}\Bigg[\frac{\exp(-\xi R/c)}{R} + 2\sum_{s=1}^{\infty}\frac{\exp(-\frac{\xi}{c}R_{os})}{R_{os}} + 2\sum_{r=1}^{\infty}\frac{\exp(-\frac{\xi}{c}R_{ro})}{R_{ro}}$$

$$-\sum_{s=-\infty}^{\infty}\frac{\exp(-\frac{\xi}{c}R_{os+})}{R_{os+}} - \sum_{r=-\infty}^{\infty}\frac{\exp(-\frac{\xi}{c}R_{+ro})}{R_{+ro}}$$

$$+4\sum_{r=1}^{\infty}\sum_{s=1}^{\infty}\frac{e^{-\frac{\xi}{c}R_{rs}}}{R_{rs}} - \sum_{r=-\infty}^{\infty}{}_{\neq 0}\sum_{s=-\infty}^{\infty}\frac{e^{-\frac{\xi}{c}R_{rs+}}}{R_{rs+}}$$

$$-\sum_{r=-\infty}^{\infty}\sum_{s=\infty}^{\infty}{}_{\neq 0}\frac{e^{-\frac{\xi}{c}R_{+rs}}}{R_{+rs}} + \sum_{r=-\infty}^{\infty}\sum_{s=-\infty}^{\infty}\frac{e^{-\frac{\xi}{c}R_{+rs+}}}{R_{+rs+}}\Bigg]$$

(4.30)

Note in equation (4.30) that the free space Green function is exhibited explicitly. Proceeding now as in section 3.3 in rewriting the sums of exponentials and construction of the diadic we obtain once more two limiting cases.

For $R\omega_0/c << 1$ and $a, b << \lambda_0$ we obtain

$$E(R) = E_L(R)\Big[1 + \frac{3}{2\pi}\Big(\frac{c}{\omega_0 L}\Big)\Big\{\Big[\frac{3(x_1-x_2)^2}{R^2}-1\Big]\Big(\frac{R}{a}\Big)^3\zeta(4) + \Big[\frac{3(y_1-y_2)^2}{R^2}-1\Big]\Big(\frac{R}{b}\Big)^3\zeta(4)$$

$$+ O\Big(\frac{R}{a,b}\Big)^5\Big\}\Big]$$

(4.31)

When $R\omega_0/c >> 1$ and a, b $>> \lambda_0$ we have

$$E(R) = E_{CP}(R)\Big[1 + \frac{2}{69}R^4\zeta(4)\Big\{\Big[\frac{3(x_1-x_2)^2}{R^2}-1\Big] + \Big[\frac{3(y_1-y_2)^2}{R^2}-1\Big]\Big\}$$

$$+ O\Big(\frac{R}{a,b}\Big)^6\Big]$$

(4.32)

CHAPTER 5

5.1 The Green Function

When the oscillators are embedded in a dielectric slab it is convenient to construct the Green Function by another method [43]. We consider the situation where we have two semi-infinite slabs of dielectric (1 and 3) separated by a slab (2) of thickness L. We choose axes in which the origin lies on the 1-2 interface and the positive z-axis is directed towards the 2-3 interface and is perpendicular to both interfaces.

The equation that $G^{(1)}(\underset{\sim}{r}, \underset{\sim}{r}')$ satisfies is then

$$\nabla^2 G^{(1)}(\underset{\sim}{r}, \underset{\sim}{r}') = \delta(\underset{\sim}{r} - \underset{\sim}{r}') \qquad (5.1)$$

with boundary conditions that $G^{(1)}$ and $\epsilon \frac{\partial G^{(1)}}{\partial z}$ be continuous across the boundaries. Now have that E_z, the normal component of the electric field, (also $\propto -\frac{\partial G^{(1)}}{\partial z}$) is discontinuous across the interfaces. Let A(x,y) and B(x,y) denote the jumps in E_z at the 1-2 and 2-3 interfaces respectively. Then the electrostatic potential $G^{(1)}$ is equivalent to that arising from a point charge immersed in an infinite medium 2 together with that due to surface charge densities A(x,y) and B(x,y) at the boundaries (we are taking $0 < z' < L$ at present). With this equivalence we are able to write

$$G^{(1)}(\underset{\sim}{r}, \underset{\sim}{r}') = g(\underset{\sim}{r}, \underset{\sim}{r}') + \int g(\underset{\sim}{r}, \underset{\sim}{r}'')\left[A(x'', y'')\delta(z'') + B(x'', y'')\delta(z'' - L)\right] d^3 r'' \qquad (5.2)$$

with

$$g(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_2 |\underset{\sim}{r} - \underset{\sim}{r}'|} = \frac{-1}{4\pi\epsilon_2 R} \qquad (5.3)$$

The potential $G^{(1)}$ is now automatically continuous across the interfaces. Imposing the remaining boundary condition that

$$\lim_{z \to 0^-} \epsilon_1 \frac{\partial G^{(1)}}{\partial z} = \lim_{z \to 0^+} \epsilon_2 \frac{\partial G^{(1)}}{\partial z}$$

$$\text{and} \quad \lim_{z \to L^-} \epsilon_2 \frac{\partial G^{(1)}}{\partial z} = \lim \epsilon_3 \frac{\partial G^{(1)}}{\partial z} \tag{5.4}$$

and using the identity

$$\lim_{z \to 0^\pm} \frac{z}{\left[(x-x'')^2 + (y-y'')^2 + z^2\right]^{3/2}} = \pm 2\pi\, \delta(x-x')\,\delta(y-y') \tag{5.5}$$

gives two simultaneous integral equations for A and B, viz.

$$\frac{-(\epsilon_1 - \epsilon_2) z'}{\left[(x-x')^2 + (y-y')^2 + z'^2\right]^{3/2}} - 2\pi(\epsilon_1 + \epsilon_2) A(x,y)$$

$$= (\epsilon_1 - \epsilon_2) L \iint_{-\infty}^{\infty} \frac{dx''dy''\, B(x'' y'')}{\left[(x-x'')^2 + (y-y'')^2 + L^2\right]^{3/2}} \tag{5.6}$$

and

$$\frac{(\epsilon_3 - \epsilon_2)(L - z')}{\left[(x-x')^2 + (y-y')^2 + (L-z')^2\right]^{3/2}} + 2\pi(\epsilon_3 + \epsilon_2) B(x,y)$$

$$= -(\epsilon_3 - \epsilon_2) L \iint_{-\infty}^{\infty} \frac{dx''dy''\, A(x'', y'')}{\left[(x-x'')^2 + (y-y'')^2 + L^2\right]^{3/2}} \tag{5.7}$$

We solve these equations by means of Fourier transforms.

Defining

$$A(k_1, k_2) = \frac{1}{(2\pi)^2} \iint_{-\infty}^{\infty} dx\,dy\, A(x,y)\, e^{-i(k_1 x + k_2 y)} \tag{5.8}$$

with a similar definition for B we then have from equations (5.6) and (5.7)

$$A(k_1,k_2) = \frac{1}{(2\pi)^2}\frac{\left(-\Delta_{12}\,\mathrm{sgn}(z')e^{-\chi|z'|} + \Delta_{12}\Delta_{32}\,\mathrm{sgn}(L-z')e^{-\chi[L+|L-z'|]}\right)}{1-\Delta_{12}\Delta_{32}e^{-2\chi L}} \qquad (5.9)$$

$$B(k_1,k_2) = \frac{1}{(2\pi)^2}\frac{\left(-\Delta_{32}\,\mathrm{sgn}(L-z')e^{-\chi|L-z'|} + \Delta_{12}\Delta_{32}\,\mathrm{sgn}(z')e^{-\chi[L+|z'|]}\right)}{1-\Delta_{12}\Delta_{32}e^{-2\chi L}} \qquad (5.10)$$

where $\Delta_{ij} = \dfrac{\epsilon_i-\epsilon_j}{\epsilon_i+\epsilon_j}$, $\chi = (k_1^2+k_2^2)^{1/2}$, $\mathrm{sgn}(z) = \begin{cases} \dfrac{z}{|z|} & z \neq 0 \\ 0 & z = 0 \end{cases}$

From these two equations A(x,y) and B(x,y) are determined. Substituting into equation (5.2) we find, on changing into polar co-ordinates in k space and carrying out the angular integration, that

$$G(\underline{r},\underline{r}') = \frac{-1}{4\pi\epsilon_2}\left\{\frac{1}{R} + \int_0^\infty \frac{d\chi\, J_0(\chi\rho)}{1-\Delta_{12}\Delta_{32}e^{-2\chi L}} \times F(\chi; z, z')\right\} \qquad (5.11)$$

where

$$F(\chi; z, z') = \left\{\mathrm{sgn}(z')\left(\Delta_{12}\Delta_{32}e^{-\chi(L+|z'|+|L-z|)} - \Delta_{12}e^{-\chi(|z|+|z'|)}\right)\right.$$

$$\left. + \,\mathrm{sgn}(L-z')\left(\Delta_{12}\Delta_{32}e^{-\chi(L+|L-z'|+|z|)} - \Delta_{32}e^{-\chi(|L-z|+|L-z'|)}\right)\right\} \qquad (5.12)$$

The removal of the restriction on the position of $\underset{\sim}{r}'$ results in an immediate generalisation. The factor $\frac{1}{\epsilon_2}$ outside the curly brackets in equation (5.11) is replaced by

$$\frac{1}{\epsilon_2} \rightarrow \left[\frac{\theta(-z')}{\epsilon_1} + \frac{\theta(z')\theta(l-z')}{\epsilon_2} + \frac{\theta(z'-L)}{\epsilon_3} \right] \equiv H(z') \tag{5.13}$$

where $\theta(z)$ is the step function to give

$$G(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{-H(z')}{4\pi} \left\{ \frac{1}{R} + \int_0^\infty \frac{dx\, J_0(x\rho)}{1 - \Delta_{12}\Delta_{32} e^{-2xL}} \times F(x;z,z') \right\} \tag{5.14}$$

5.2 Interaction in the Non-Retarded Limit

From equation (5.12) we note that the form of the function $F(\varkappa;z,z')$ will be considerably altered according to the relative positions of the two oscillators, in particular their positioning with regards their z co-ordinate.

We consider firstly the case for which L is large. Taking the situation in which both oscillators are between the two dielectric boundaries i.e. $0 < z, z' < L$, use of equation (5.12) then gives us

$$F(\varkappa;z,z') = \Big\{ \Delta_{12}\Delta_{32}\exp[-\varkappa(2L-(z-z'))] - \Delta_{12}\exp[-\varkappa(z+z')] + \Delta_{12}\Delta_{32}\exp[-\varkappa(2L+(z-z'))] - \Delta_{32}\exp[-\varkappa(2L-(z+z'))] \Big\} \tag{5.15}$$

Substituting now into equation (5.14) we expand the denominator in the integral as a power series and, assuming $z > z'$ retain terms to order $\exp[-\varkappa L]$ to get

$$G(\underset{\sim}{r},\underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_2}\Big\{ \frac{1}{R} + \int_0^\infty d\varkappa \, J_0(\varkappa\rho) \times \Big[-\Delta_{12}e^{-\varkappa(z+z')} + \Delta_{12}\Delta_{32}e^{-\varkappa(2L-(z-z'))} - \Delta_{32}e^{-\varkappa(2L-(z+z'))} \Big] \Big\} \tag{5.16}$$

The second and third terms in the square brackets in equation (5.16) are retained initially since in certain configurations these terms will be of order $\exp(-\varkappa L)$.

When the oscillators are near the middle of the two interfaces, we retain all the terms in equation (5.16) and using the formula

$$\int_0^\infty d\kappa \, J_0(\kappa\rho)\, e^{-\kappa a} = \left(\rho^2 + a^2\right)^{-1/2} \qquad a > 0 \tag{5.17}$$

we obtain

$$G(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_2}\left\{ \frac{1}{R} - \frac{\Delta_{12}}{R_+} - \frac{\Delta_{32}}{R_{L+}} + \frac{\Delta_{12}\Delta_{32}}{R_L} \right. \tag{5.18}$$

where $R_+^2 = \rho^2 + (z+z')^2$, $R_{L+}^2 = \rho^2 + (2L - (z+z'))^2$

$$R_L^2 = \rho^2 + (2L - (z-z'))^2 \tag{5.19}$$

Use now of equations (3.26) and (2.23) gives us

$$\begin{aligned} E(R) = \frac{1}{\epsilon_2^2} E_L(R)\Big\{ 1 &- \frac{R^3}{3}\left[\frac{\Delta_{12}}{R_+^3} + \frac{\Delta_{32}}{R_{L+}^3} - \frac{3\Delta_{12}\Delta_{32}}{R_L^3} \right] \\ &- \frac{R}{3}\left[\frac{3\Delta_{12}\left(\rho_{12}^4 - (z_1-z_2)^2(z_1+z_2)^2\right)}{R_+^5} + \frac{3\Delta_{32}\left(\rho_{12}^4 - (z_1-z_2)^2(2L-(z_1+z_2))^2\right)}{R_{L+}^5} \right. \\ &\left. \qquad - \frac{9\Delta_{12}\Delta_{32}\left(\rho_{12}^4 + (z_1-z_2)^2(2L-(z_1-z_2))^2\right)}{R_L^5} \right] \\ &+ R^6\left[\frac{\Delta_{12}^2}{R_+^6} + \frac{\Delta_{32}^2}{R_{L+}^6} + \frac{\Delta_{12}^2\Delta_{32}^2}{R_L^6} \right] \Big\} \end{aligned} \tag{5.20}$$

where $E_L(R)$ is as previously defined.

When both oscillators are near one of the interfaces i.e. $z_1 - z_2 << L$ we have

$$G(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_2}\left\{ \frac{1}{R} - \frac{\Delta_{12}}{R_+} - \frac{\Delta_{32}}{R_{L+}} \right\} \tag{5.21}$$

which gives us

$$E(R) = \frac{1}{\epsilon_2^2} E_L(R)\Big\{ 1 - \frac{R^3}{3}\Big[\frac{\Delta_{12}}{R_+^3} + \frac{\Delta_{32}}{R_{L+}^3} \Big] \tag{5.22}$$

$$- R\Big[\Delta_{12}\frac{(\rho_{12}^4 - (z_1 - z_2)^2 (z_1 + z_2)^2)}{R_+^5} + \Delta_{32}\frac{(\rho_{12}^4 - (z_1 - z_2)^2 (2L - (z_1 + z_2))^2)}{R_{L+}^5}$$

$$+ R^6\Big[\frac{\Delta_{12}^2}{R_+^6} + \frac{\Delta_{32}^2}{R_{L+}^6} \Big] \Big\}$$

Equations (5.21) and (5.22) should be compared to the corresponding results for two oscillators near a single interface (obtained by putting $\epsilon_2 = \epsilon_3$ in equation (5.16))

$$G(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_2}\left\{ \frac{1}{R} - \frac{\Delta_{12}}{R_+} \right\} \tag{5.23}$$

$$E(R) = \frac{1}{\epsilon_2^2} E_L(R)\Big\{ 1 - \frac{\Delta_{12}}{3}\frac{R^3}{R_+^3} - \Delta_{12} R\frac{[\rho_{12}^4 - (z_1 - z_2)^2 (z_1 + z_2)^2]}{R_+^5} + \Delta_{12}^2 \frac{R^6}{R_+^6} \Big\} \tag{5.24}$$

If now we have one oscillator each side of the 1-2 interface then we have

$$F(\kappa, z, z') = \Big\{ \Delta_{12} e^{-\kappa(z - z')} - \Delta_{12}\Delta_{32} e^{-\kappa(2L - (z + z'))} + \Delta_{12}\Delta_{32} e^{-\kappa(2L + (z - z'))} - \Delta_{32} e^{-\kappa(2L - (z + z'))} \Big\} \tag{5.25}$$

which gives, proceeding as before

$$G(\underset{\sim}{r},\underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_1}\left\{\frac{1}{R} + \int_0^\infty \underline{dx\, J_0(x\rho)}\left[\Delta_{12} e^{-x(z-z')} - \Delta_{32}(1+\Delta_{12}) e^{-x(2L-(z+z'))}\right]\right\} \tag{5.26}$$

If both oscillators are near the 1-2 interface then we have

$$G(\underset{\sim}{r},\underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_1}\left\{\frac{(1+\Delta_{12})}{R}\right\} \tag{5.27}$$

and E(R) = $\frac{1}{\epsilon_1^2} E_L(R)\,(1+\Delta_{12})^2$ (5.28)

$$= \frac{E_L(R)}{(\epsilon_1^2+\epsilon_2^2)^2}$$

However if the first oscillator is near the 2-3 interface then we have from equation (5.26)

$$G(\underset{\sim}{r},\underset{\sim}{r}') = \frac{-1}{4\pi\epsilon_2}\left\{(1+\Delta_{12})\frac{1}{R} - \frac{\Delta_{32}(1+\Delta_{12})}{R_{L+}}\right\} \tag{5.29}$$

to give

$$E(R) = E_L(R)\left\{\frac{1}{(\epsilon_1+\epsilon_2)^2} - \frac{2\Delta_{32}}{(\epsilon_1+\epsilon_2)}\left[\frac{R^3}{R_{L+}^3} + \frac{3(\rho_{12}^4-(z_1-z_2)^2(2L-(z_1+z_2))^2)R}{R_{L+}^5}\right]\right.$$
$$\left. + \Delta_{32}^2(1+\Delta_{12})^2\frac{R^6}{R_{L+}^6}\right\} \tag{5.30}$$

which is the result of equation (5.28) plus a correction term due to the proximity of the 2-3 interface to the first oscillator.

When the oscillators are placed one in region 1 and one in region 3, both near the interfaces we have

$$F(\kappa; z, z') = (\Delta_{12} - \Delta_{12}\Delta_{32} - \Delta_{32})e^{-\kappa(z-z')} + \Delta_{12}\Delta_{32}\, e^{-\kappa(2L+(z-z'))} \tag{5.31}$$

and working as before

$$G(\underset{\sim}{r}, \underset{\sim}{r}') = -\frac{1}{4\pi\epsilon_1}\left\{\frac{1 + \Delta_{12} - \Delta_{12}\Delta_{32} - \Delta_{32}}{R}\right\} \tag{5.32}$$

and

$$E(R) = E_L(R)\left[\frac{4\epsilon_2}{(\epsilon_1 + \epsilon_2)(\epsilon_2 + \epsilon_3)}\right]^2 \tag{5.33}$$

Turning now our attention to the case when L is small, we write the denominator of the integral in equation (5.14) as

$$\left(1 - \Delta_{12}\Delta_{32}e^{-2\kappa L}\right)^{-1} = \left[1 - \Delta_{12}\Delta_{32}\left(1 - 2\kappa L + \frac{(2\kappa L)^2}{2!} \cdots\right)\right]^{-1}$$

$$= (1 - \Delta_{12}\Delta_{32})^{-1}\left[1 + \frac{\Delta_{12}}{1 - \Delta_{12}\Delta_{32}}\left(2\kappa L - \frac{(2\kappa L)^2}{2!} \cdots\right)\right]^{-1}$$

$$= (1 - \Delta_{12}\Delta_{32})^{-1}\left[1 - \frac{\Delta_{12}\Delta_{32}}{1 - \Delta_{12}\Delta_{32}} \cdot 2\kappa L \cdots\right] \tag{5.34}$$

This then enables us to write

$$G(\underset{\sim}{r}, \underset{\sim}{r}') = \frac{-H(z')}{4\pi}\left\{\frac{1}{R} + (1 - \Delta_{12}\Delta_{32})^{-1}\int_0^\infty J_0(\kappa\rho)\, d\kappa\, F(\kappa; z, z')\left[1 - \frac{\Delta_{12}\Delta_{32}}{1 - \Delta_{12}\Delta_{32}} \cdot 2\kappa L \cdots\right]\right. \tag{5.35}$$

With the oscillators in the slab i.e. $0 < z, z' < L$ expanding the function F in power series and retaining leading terms we get

$$G(\underline{r}, \underline{r}') = \frac{1}{4\pi\epsilon_2}\left\{\frac{1}{R} + \frac{(2\Delta_{12}\Delta_{32} - \Delta_{12} - \Delta_{32})}{(1 - \Delta_{12}\Delta_{32})\rho}\right\} \tag{5.36}$$

which yields

$$E(R) = \frac{1}{\epsilon_2} E_L(R)\left\{1 + \frac{R}{\rho_{12}}\left[\frac{\Delta_{12}(\Delta_{32}-1) + \Delta_{32}(\Delta_{12}-1)}{1 - \Delta_{12}\Delta_{32}}\right] \times \left[5 - \frac{(z_1 - z_2)^2}{\rho_{12}^2}\right]\right\} \tag{5.37}$$

When the oscillators are located either side of the thin slab we have

$$G(\underline{r}, \underline{r}') = \frac{1}{4\pi\epsilon_1}\left\{\frac{1}{R} + \frac{\Delta_{12} - \Delta_{32}}{(1 - \Delta_{12}\Delta_{32})\rho}\right\} \tag{5.38}$$

giving the energy of the interaction as

$$E(R) = \frac{1}{\epsilon_1} E_L(R)\left\{1 + \frac{R}{6\rho_{12}}\left(5 - \frac{(z_1 - z_2)^2}{\rho_{12}^2}\right)\left[\frac{\Delta_{12} - \Delta_{32}}{1 - \Delta_{12}\Delta_{32}}\right]\right\} \tag{5.39}$$

We note that the results of equation (5.24) agree with the zero temperature limit of the results obtained by Richmond and Sarkies [47] for the free energy of interaction between two oscillators in a similar physical environment.

CHAPTER 6

In this chapter we turn our attention briefly to the resonance interaction between two oscillating dipoles. This situation arises when two molecules, one in an excited state, the other in the ground state, interact with each other, the excitation energy being transferred from one to the other in rapid succession [48].

In line with the semi-classical ideas developed in this work, the process can be interpreted as the energy of one oscillating dipole in the radiation field of the other [49, 50]. We consider the radiation pattern of an oscillating dipole at $\underset{\sim}{R}_1$, frequency $(+w_o)$, and the energy in the resulting electric field of another oscillating dipole with the same amplitude, but frequency $(-w_o)$ located at $\underset{\sim}{R}_2$. The change in sign of the frequency is consistent with the quantum mechanical description of the interaction as the adsorption of a photon by one molecule after its emission by the other.

The electric field due to the first dipole can be written as

$$\underset{\sim}{\mathcal{E}}(\underset{\sim}{r}, t) = \frac{4\pi\omega_o^2}{c^2} \exp(i\omega_o t)\, \underset{=}{G}^{(2)}(\underset{\sim}{r}, \underset{\sim}{R}_1; \omega_o) \cdot \underset{\sim}{p}_1 \tag{6.1}$$

where $\underset{\sim}{p}_1$ is the dipole moment amplitude of the first dipole and $\underset{=}{G}^{(2)}$ is the diadic Green function for the electric field wave equation with appropriate boundary conditions [51]. The expression for the transferred energy is therefore

$$E(R) = -\left\{\underset{\sim}{p}_2 \exp(-i\omega_o t)\right\} \cdot \underset{\sim}{\mathcal{E}}(\underset{\sim}{R}_2, t)$$

$$= -\frac{4\pi\omega_o^2}{c^2}\left\{\underset{\sim}{p}_2 \cdot \underset{=}{G}^{(2)}(\underset{\sim}{R}_2, \underset{\sim}{R}_1; \omega_o) \cdot \underset{\sim}{p}_1\right\} \tag{6.2}$$

where $R = |\underset{\sim}{R}_2 - \underset{\sim}{R}_1|$.

We see from equation (6.2) that it is the diadic Green function $\underline{\underline{G}}^{(2)}$ which determines the R- dependence of the energy of the interaction.

If we consider firstly a duct of the type dealt with in chapter 4, then the diadic Green function is given by equation (4.7). For simplicity we take the two oscillators to lie on the axis of the duct, i.e. $x_1 = x_2 = a/2$, $y_1 = y_2 = b/2$, and then $R = |z-z'|$.

The typical element we then have to consider is

$$G_{nm}(R,\omega) \approx \frac{2}{\pi ab} \int_{-\infty}^{\infty} \frac{dk\, e^{ikR}}{\left[\frac{\omega^2}{c^2} - \left(\frac{n^2\pi^2}{a^2} + \frac{m^2\pi^2}{b^2}\right)\right] g(k)} \tag{6.3}$$

where g(k) has no zeroes for k real. Evaluating G_{nm} by contour integration methods [39] we will have (closing the contour in the upper half plane)

$$G_{nm}(R,\omega) = 2\pi i \sum (\text{residues in upper half plane})$$

$$+ \pi i \sum (\text{residues of poles on real axis})$$

where this is a Principal Value evaluation of the integral.

Any residue enclosed by the contour in the upper half plane will contribute a term of the form $\exp(-\alpha R), \alpha > 0$ which for large R we neglect. Hence the only terms of interest are those arising from poles on the real axis. When a,b are of the order of the wavelength $\lambda_0 = \frac{2\pi c}{\omega_0}$

$$\gamma_{nm} = \left[\frac{\omega_0^2}{c^2} - \left(\frac{n^2\pi^2}{a^2} + \frac{m^2\pi^2}{b^2}\right)\right]^{1/2} \tag{6.4}$$

will be real for only the lowest order terms. Returning now to equation (4.7) we see that only one term is both non-zero and of interest to us, namely

$$\underline{\underline{G}}^{(2)}(\underline{r},\underline{r}',\omega_0)\Big|_{33} = \frac{2}{\pi ab}\,\underline{a}_3\underline{a}_3 \int_{-\infty}^{\infty} \frac{dk\, e^{ikR}\left(\frac{\pi^2}{a^2}+\frac{\pi^2}{b^2}\right)}{(\gamma_{11}^2 - k^2)\left(k^2+\frac{\pi^2}{a^2}+\frac{\pi^2}{b^2}\right)} \tag{6.5}$$

$$= \frac{2c^2}{ab\,\omega_0^2}\;\frac{\sin(\gamma_{11}R)}{\gamma_{11}} + \text{terms of type } e^{-\alpha R}$$

Using equation (6.5) in equation (6.2) we see that E(R) has the form

$$E(R) \approx \frac{C.\sin(\gamma_{11}R)}{ab\,\gamma_{11}} \tag{6.6}$$

which represents a considerable enhancement from the free space result [50]

$$E(R) \approx C_1\,\frac{\cos\left(\frac{\omega_0 R}{c}\right)}{R} \tag{6.7}$$

As a second example we consider the situation of Chapter 3, the oscillators between metallic plates for which the Green function diadic is given by equation (3.14), where we again take L to be of the order of $\lambda_0 = 2\pi c/\omega_0$. Proceeding in a similar manner to that just outlined we find that terms of importance have the form

$$G(R,\omega_0) \approx C_3\,\frac{\sin(k_0R - \frac{1}{4}\pi)}{(k_0R)^{1/2}} \tag{6.8}$$

giving

$$E(R) \approx \frac{C_4\sin(k_0R - \frac{1}{4}\pi)}{(k_0R)^{1/2}} \tag{6.9}$$

where $k_0^2 = \left(\frac{\omega^2}{c^2} - \frac{\pi^2}{L^2}\right)$

Equation (6.9) also represents an enhancement from the free space value.

These examples illustrate that the alteration of the radiation field in a bounded region, seen in the alteration of the Green function diadic for the electric field, can markedly influence the resonance interaction process.

CHAPTER 7

Scrutiny of the results for the three physical configurations considered here reveal that, in some instances, quite marked alterations to the interaction between molecules can occur due entirely to the boundaries of the physical situation in which the molecules are placed. In the formalism used here these effects are seen to enter via the alteration of some or all modes in the two Green functions (scalar and diadic) for the scalar and vector potentials for the electric field.

While we have seen that the semi-classical formalism used here provides a simple formulation for the problem of the interaction between oscillating dipoles, it readily becomes apparent that the situation can become complex if arbitrary shaped containers with mixed types of boundaries are considered. The difficult part then becomes the calculation of the two Green functions and their subsequent manipulation to obtain meaningful results for the interaction energy.

Of the three cases considered in this work, the dielectric slab configuration although being more difficult with regards the computation of the Green functions tends to show the smaller departures from the free space results, due mainly to the fact that dielectric boundary conditions do not produce the massive discretization of modes that occurs with perfectly conducting walls, hence the deviations from free space values are not so marked. Examination of the results of chapter 5 will reveal that the dielectric properties of the materials are also capable of altering the nature of the interaction via means of the dielectric differences

In the cases of the perfectly conducting wall situations of chapters 3 and 4, we see in some of the results situations where enhancement from free space results can arise while in others a degradation is evident. The duct model of chapter 4 is an important beginning for modelling of waveguides and the processes occurring with them.

The enhancement of the resonance transfer process as evidenced by equations (6.6) and (6.9) may play an important part in biological system in excitonic energy transfer [50]. For the excitation of a molecule or radical, the characteristic wavelength of the radiation involved is much larger than its size. Hence if the molecule is in an inhomogeneously distributed material where the characteristic length of the inhomogenity of the distribution is of the order of this characteristic wavelength it is possible for a strong channelling effect to occur in certain directions giving a great efficiency in resonant energy transfer in those directions.

Extensions of this work occur in several directions. Since this work was begun, the semi-classical formalism, here used to treat only the dipole-dipole part of the interaction, has been extended using perturbation methods to produce a theory which readily allows inclusion of higher order multipole interactions [52].

Extension of dispersion force theory has already begun to include finite size molecules, giving rise to non-divergent self energies and two particle interactions at zero-limit separation [53]. It is worthwhile to note that Richardson [52] also obtains non-divergent zero-limit interactions when higher order multipole interactions are considered.

Further avenues for exploration are opened up when spatially dispersive media are involved. It is in these directions that this work will be carried in an endeavour to obtain a better understanding of the dispersion interactions occurring in the real world.

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