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Recoil Saturation of the Self-Energy in Atomic Systems

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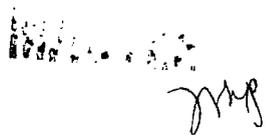
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Abstract

Within the framework of the general self-energy problem for the interaction of a projectile with a many-body system, we consider the dispersion force between two atoms or between a charge and an atom. Since the Born-Oppenheimer approximation is not made, this is a useful approach for exhibiting non-adiabatic effects. We find compact expressions in terms of matrix elements of operators in the atomic displacement which are not limited by multipole expansions.

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There are many instances in physics where one wishes to study the interaction of a projectile with a many-particle target. In fact the projectile itself may also have a composite structure such as the case of an atom or molecule. It is often extremely useful to reduce this inherent many-body problem to an effective single particle problem, usually expressed as a function of the center-of-mass coordinates of the system.

Examples of such systems include the interaction of a charge Q with a conducting surface, in which case the long-range interaction is described by the classical image potential in the distance z from the surface

$$V(z) = -Q^2/4z \quad (1)$$

For an atom or molecule interacting with the surface the corresponding interaction is given by the Van der Waals potential

$$V(z) = -C_3/z^3 \quad (2)$$

In this paper we wish to discuss the interaction between a charge and an atom where the long range potential in the separation distance R is the polarization force term:

$$V(R) = -\alpha Q^2/R^4 \quad (3)$$

We also address the closely related problem of the interaction between two atoms, which at large distances is the Van der Waals dispersion potential

$$V(R) = -C_6/R^6 \quad (4)$$

A time honored method for treating such complex problems which has been extensively applied in solid state physics is to reduce the many body problem to the solution of an effective Schrödinger equation with a non-local potential operator called the self-energy^{1,2)}

$$\left\{ \frac{\hbar^2}{2m} \nabla^2 + u(\underline{r}) \right\} \psi_0 + \int d\underline{r}' \Sigma(\underline{r}, \underline{r}', E_0) \psi_0(\underline{r}') = E_0 \psi_0(\underline{r}) \quad (5)$$

The potential $u(\underline{r})$ includes any local potentials which are treatable separately from the non-local self-energy $\Sigma(\underline{r}, \underline{r}', E_0)$. This can be further forced into the form of a local Schrödinger equation by imposing the following condition:

$$\Sigma_0(\underline{r}) \psi_0(\underline{r}) = \int d\underline{r}' \Sigma(\underline{r}, \underline{r}', E_0) \psi_0(\underline{r}') \quad (6)$$

This leads to an effective Schrödinger equation in the self-energy $\Sigma_0(\underline{r})$ of the form

$$\left\{ \frac{\hbar^2}{2m} \nabla^2 + u(\underline{r}) + \Sigma_0(\underline{r}) \right\} \psi_0(\underline{r}) = E_0 \psi_0(\underline{r}) \quad (7)$$

We note that the nonlocal self-energy depends on the energy of the system, while the local self-energy of Eq. (6) depends not only on the energy but also on the initial state $\psi_0(\underline{r})$

We have developed a method for determining a self-energy which, although somewhat different from that of Refs. (1) and (2), is much simpler and in many cases leads to equivalent results. The method is based on perturbation theory, and in particular on the energy shift of an unperturbed state of the system,

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$$\Delta E_0 = \sum_l \frac{\langle 0 | H' | l \rangle \langle l | H' | 0 \rangle}{E_l - E_0 - i\delta} + \dots \quad (8)$$

where an unperturbed state $|l\rangle$ is of the product form

$$|l\rangle = \phi_l(\underline{r}) |l\rangle |n_l\rangle \quad (9)$$

with $\phi_l(\underline{r})$ a center-of-mass spatial wavefunction, $|l\rangle$ is the internal state of the projectile and $|n_l\rangle$ is the many body state of the target. The energy shift can be rewritten as the integral over the local self-energy weighted by the probability of finding the system in the initial center-of-mass state

$$\Delta E_0 = \int d\underline{r} \phi_0(\underline{r}) \Sigma_0(\underline{r}) \phi_0(\underline{r}) \quad (10)$$

Comparison of Eq. (10) with Eq. (8) leads to our definition of the self-energy.³⁾ This self-energy is in general complex. The imaginary part can be subdivided into a conservative and a nonconservative part. The nonconservative part can be used to describe real transitions and energy exchange in the system.⁴⁾

We consider here the application of this method to the interaction of two atoms or of a charge with an atom. We begin by discussing the interaction between two hydrogen-like atoms, and the case of a charge interacting with an atom will be shown later to be very similar. For simplicity, we neglect exchange. The unperturbed system of two isolated atoms has an eigenstate consisting of the product of two atomic functions and a momentum function in the relative coordinate \underline{R} between their centers of mass

$$|j\rangle = |n_j\rangle |l_j\rangle \phi_j(\underline{R}) = |n_j\rangle |l_j\rangle \phi_j(\underline{R}) \quad (11)$$

The momentum function is a plane wave $\phi_j(\underline{R}) \propto \exp(i\underline{Q}_j \cdot \underline{R})$ and the unperturbed energy is

$$E_j = \varepsilon_{l_j} + \varepsilon_{n_j} + Q_j^2/2\mu \quad (12)$$

where ε_{l_j} and ε_{n_j} are atomic energies measured from the ground state and

μ is the reduced mass of the two atom system

$$\mu = (m_1+1)(m_2+1)/(m_1+m_2+2) \quad (13)$$

If \underline{r}_1 and \underline{r}_2 are the respective atomic displacement operators, the perturbation contribution to the Hamiltonian is

$$H' = \sum_{i=1}^4 (-1)^i |\underline{R} - \underline{R}_i|^{-1} \quad (14)$$

with the \underline{R}_i given by

$$\underline{R}_1 = \underline{r}_1/(m_1+1) + m_2\underline{r}_2/(m_2+1)$$

$$\underline{R}_2 = -m_1\underline{r}_1/(m_1+1) + m_2\underline{r}_2/(m_2+1) \quad (15)$$

$$\underline{R}_3 = -m_1\underline{r}_1/(m_1+1) - \underline{r}_2/(m_2+1)$$

$$\underline{R}_4 = \underline{r}_1/(m_1+1) - \underline{r}_2/(m_2+1)$$

The \underline{R}_i above are expressed in center-of-mass coordinates and the four terms in Eq. (4) correspond to the four different potential terms arising from the interaction of the electron or nucleus of one atom with the electron or nucleus of the other atom.

The lowest order contribution to $\Sigma_0(\underline{R})$ comes from second order perturbation theory and is given by

$$\Sigma_0^a(\underline{R}) = \sum_j \frac{\phi_j(\underline{R})}{\phi_0(\underline{R})} \frac{\langle 00 | \hat{H} | n_j \ell_j \rangle \langle j | \hat{H} | 0 \rangle}{E_0 - E_j} \quad (16)$$

The matrix elements represented by angular brackets $\langle \rangle$ are taken with respect to atomic states only, while those represented by $()$ include also the state of relative motion, as shown in Eq. (11). After Fourier expansion of the perturbation (14), the matrix elements can be partially evaluated to put the self-energy in the form of a sum over atomic matrix elements of generalized atomic operators

$$\Sigma_0^a(\underline{R}) = \frac{1}{2\pi^2} \sum_{\ell} \sum_n \langle 00 | \hat{H} | \ell n \rangle \langle n \ell | \tilde{I} | 00 \rangle \quad (17)$$

where

$$\tilde{I} = \sum_{i=1}^4 (-1)^i \int (d\underline{Q}/Q^2) e^{i\underline{Q} \cdot (\underline{R} - \underline{R}_i)} (\epsilon_{\ell+} \epsilon_n + [Q_o^2 - (\underline{Q}_o + \underline{Q})^2] / 2\mu)^{-1} \quad (18)$$

If we now make the lowest order expansion in terms of the parameter R_i/R all results obtained previously for two atoms interacting in the dipole limit are recovered. For the case of identical atoms this asymptotic form is

$$\Sigma_0(\underline{R}) = \frac{1}{R^6} \sum_{f,g} \frac{|Q_{fg}|^2}{(\epsilon_f + \epsilon_g)} \left\{ 1 + \frac{6 k_o}{(m+1)(\epsilon_f + \epsilon_g)} \frac{1}{R} - \frac{48 k_o^2}{(m+1)^2 (\epsilon_f + \epsilon_g)^2} \frac{1}{R^2} + \dots \right\} \quad (19)$$

where Q_{fg} is the combination of atomic matrix elements

$$Q_{fg} = 2 \langle f | z_1 | 0 \rangle \langle g | z_2 | 0 \rangle - \langle f | x_1 | 0 \rangle \langle g | x_2 | 0 \rangle - \langle f | y_1 | 0 \rangle \langle g | y_2 | 0 \rangle \quad (20)$$

The leading term is the familiar Van der Waals contribution,⁵⁾ the next term is a conservative imaginary contribution^{6,7)}, and the term in k_o^2 is the well known first non-adiabatic correction.

Evaluating the operator of Eq. (18) for a general relative momentum \underline{Q}_0 of the unperturbed system is straightforward but leads to complicated forms. However, many features of the general problem can be illustrated by looking at the special limiting case of two atoms with no relative motion, $\underline{Q}_0=0$. Then all integrals can be readily evaluated to give the self-energy in the form

$$\Sigma_0^a(\underline{R}) = - \sum_{\ell} \sum_n \frac{1}{|\epsilon_{\ell} + \epsilon_n|} \langle 00 | H' | \ell n \rangle \langle \ell n | H' - \sum_{i=1}^4 (-1)^i \frac{e^{-a|\underline{R}-\underline{R}_i|}}{|\underline{R}-\underline{R}_i|} | 00 \rangle \quad (21)$$

where $a^2 = 2\mu|\epsilon_{\ell} + \epsilon_n|$. The terms exponentially decreasing in R in the second matrix element of (21) are due to the quantum mechanical recoil; specifically, they arise from the term in Q^2 in the denominator of Eq. (18). For large R Eq. (21) becomes the familiar London form of the $1/R_q^6$ van der Waals potential as is evident from Eq. (19) above. Further discussion of Eq. (21) is perhaps best deferred until we obtain below the corresponding expression for the charge-atom case where the results are somewhat simpler in form. We note in passing, however, that $\Sigma_0^a(\underline{R})$ is finite as $R \rightarrow 0$.

Moving now to the interaction between a hydrogenic atom and a charge of unit mass, the unperturbed eigenstates are products of a single atomic state and the relative momentum wave function. The perturbing potential is

$$H^q = \sum_{i=1}^2 (-1)^i \frac{1}{|\underline{R}-\underline{L}_i|} \quad (22)$$

with

$$\underline{L}_i = -\underline{r}/(m+1) ; \underline{L}_2 = m\underline{r}/(m+1) \quad (23)$$

where \underline{r} is the atomic displacement operator and \underline{R} is the vector joining the charge to the center of mass of the atom. The self-energy is again defined by Eq. (16) and can be put in a form similar to the atomic case of Eq. (17)

$$\Sigma_0^q(\underline{R}) = \frac{1}{2\pi^2} \sum_n \langle 0 | H^q | n \rangle \langle n | I' | 0 \rangle \quad (24)$$

with the atomic operator I' given by

$$I' = \int (d\underline{Q}/Q^2) e^{i\underline{Q} \cdot \underline{R}} \frac{2}{\sum_{i=1}^2 \exp(-i\underline{Q} \cdot \underline{L}_i) (\epsilon_n - [2\underline{Q} \cdot \underline{Q}_0 - Q^2]/2\mu_q)^{-1}} \quad (25)$$

where the reduced mass in this case is

$$\mu_q = (m+1)/(m+2) \quad (26)$$

Again the integrals in Eq. (25) can be carried out for all values of \underline{Q}_0 but this leads to some lengthy and cumbersome equations. The case of zero relative motion, $\underline{Q}_0=0$ leads to a simple expression in compact form similar to Eq. (21):

$$\Sigma_0^q(\underline{R}) = - \sum_n \frac{1}{|\epsilon_n|} \langle 0 | H^q | n \rangle \langle n | H^q - \sum_{i=1}^2 (-1)^i \frac{e^{-b|\underline{R}-\underline{L}_i|}}{|\underline{R}-\underline{L}_i|} | 0 \rangle \quad (27)$$

where $b^2 = 2\mu_q |\epsilon_n|$. As was pointed out for the case of Eq. (19), when Eq. (24) is developed in an expansion in large values of the separation distance R , one recovers all previously obtained results for the multipole series, beginning with the long range polarization potential which behaves as $1/R^4$. However, Eq. (24) gives us the compact form expression from which the asymptotic multipole expansion can be derived. Of interest here is the fact that the interaction self-energy is finite in the limit of small separation, as should be the case for quantum mechanical systems. Two interesting limiting cases can be readily

evaluated. For the case of positronium interacting with a charge of unit mass we have $m=1$ and the self-energy for $R=0$ is zero. On the other hand if the mass m is very large we have

$$\Sigma_0^q(0) \xrightarrow{m \rightarrow \infty} -m, \quad (28)$$

The self-energy at the origin diverges with the mass in this semi-classical limit.

We have considered here the self-energy for an atom interacting with another atom or with a charge. We show that the self-energy can be expressed in terms of matrix elements between unperturbed atomic states of closed form operators in the atomic displacement. This result in itself is of interest because it gives a compact form from which the well known asymptotic multipole expansion at large separation distances can be obtained.

Since these calculations were carried out without imposing the Born-Oppenheimer approximation, the non-adiabatic and recoil contributions are present. Recoil effects are manifest at small separation distances where they cause a saturation of the self-energy to a finite value. The range over which these saturation effects occur can be estimated from Eq. (27) where $b = \sqrt{2\mu_q \epsilon_n}$, and will be, for typical atomic excitation energies, of the order of a few atomic unit if the charge is an electron. For the case of interactions between two ordinary atoms these recoil effects are totally negligible due to the large reduced mass. However, if one or both of the atoms is a positronium atom, the reduced mass is of the order of that of an

electron and the range of the saturation effects given by

$a = \sqrt{2\mu(\epsilon_l + \epsilon_n)}$ is again of order of a few atomic units. The

saturation to a finite energy is a reflection of the fact that in interactions with a quantum-mechanical atom of finite mass both the nucleus and electron must be viewed as charge clouds and the self-energy is just the interaction energy of the corresponding overlapping charge distributions.

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