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Recoil saturation of the self-energy in atomic systems

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We consider the dispersion-interaction self-energy of two atoms or of a charge and an atom without imposing the Born-Oppenheimer approximation. We find compact expressions in terms of matrix elements of operators in the atomic displacement which are not limited by multipole expansions. The saturation effect of recoil causes the self-energy to be finite even at small separation. The relation to previously obtained results in terms of multipole expansions is discussed.

There is presently a renewed interest in the study of interacting atomic systems in which one or more of the members has very small mass, such as positronium.[1-3] In this situation, nonadiabatic effects arising from the breakdown of the Born-Oppenheimer approximation become important. At large separation distances the nonadiabatic contributions generally appear as velocity-dependent corrections to the van der Waals potential and can be developed as a series in inverse powers of the separation distance. At small separation distances the major effect of the breakdown of the Born-Oppenheimer approximation is the recoil of the atoms due to conservation of momentum during the exchange of virtual quanta. This recoil causes a weakening, or saturation, of the interaction forces.

Recently a method has been developed for treating these many-body effects in atomic interactions in a completely quantum-mechanical manner.[4] This method is based on determining the interaction self-energy from perturbation theory and can be extended to all orders in the perturbation series. In the point dipolar limit, it has been applied to the interaction of two atoms[1] or an atom and a charge,[2] in the case in which exchange is neglected. For both of these examples, in addition to determining the long-range nonadiabatic corrections, the saturation of the interaction at close range was considered. The effect is quite similar, the atomic $1/R^6$ (where R is the separation distance) van der Waals potentials is reduced to a $1/R^4$ behavior.[1,5] and the charge-atom $1/R^4$ polarization potential saturates to a $1/R^2$ form.[2,5] In both examples the interaction energy is reduced by two powers of $1/R$, but it still increases without bound at small separations, a direct result of the treatment of the atoms as dipoles. One would expect a similar behavior in each of the terms of the multipole series, but clearly this large interaction energy at small separation cannot be correct. When the mass of the nucleus is finite, its recoil as it exchanges virtual quanta will smear it out into a charge cloud. Thus the interaction of atomic systems at short distances should appear as the overlapping of charge clouds (or charge distributions) which gives rise to finite interaction energy.

In this report we show that the total interaction energy in second-order perturbation theory of a system of two hydrogenic atoms, or of an atom and a charge, can be written in terms of matrix elements of closed-form atomic operators. This is equivalent to summing the whole multipole series. In addition to reducing to previously obtained results in the appropriate limits, this new expression exhibits two interesting features. First, the interaction energy is shown to be finite at all separation distances. Second, it demonstrates that the large separation expansions of the interaction potential, which are often expressed as asymptotic series in $1/R$, can be written as finite closed-form expressions.[6]

We begin by discussing the interaction between two hydrogenlike 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 $\mathbf{R}$ between their centers of mass

$$|j)=|n_j\rangle\,|l_j\rangle\phi_j(\mathbf{R})=|n_jl_j\rangle\phi_j(\mathbf{R})\ . \tag{1}$$

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

$$E_j=\epsilon_{l_j}+\epsilon_{n_j}+Q_j^2/2\mu\ , \tag{2}$$

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

$$\mu=(m_1+1)(m_2+1)/(m_1+m_2+2)\ . \tag{3}$$

If $\mathbf{r}_1$ and $\mathbf{r}_2$ are the respective atomic displacement operators (i.e., for a hydrogenic atom $\mathbf{r}_{1,2}$ are the respective displacement vectors between the electron and the nucleus of each of the two atoms), the perturbation contribution to the Hamiltonian is

$$H'=\sum_{i=1}^{4}(-1)^i|\mathbf{R}-\mathbf{R}_i|^{-1}\,, \tag{4}$$

with the $\mathbf{R}_i$ given by

$$\begin{aligned}
\mathbf{R}_1&=\mathbf{r}_1/(m_1+1)+m_2\mathbf{r}_2/(m_2+1)\,,\\
\mathbf{R}_2&=m_1\mathbf{r}_1/(m_1+1)+m_2\mathbf{r}_2/(m_2+1)\,,\\
\mathbf{R}_3&=-m_1\mathbf{r}_1/(m_1+1)-\mathbf{r}_2/(m_2+1)\,,\\
\mathbf{R}_4&=\mathbf{r}_1/(m_1+1)-\mathbf{r}_2/(m_2+1)\,.
\end{aligned} \tag{5}$$

The $\mathbf{R}_i$ 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 interaction self-energy $\Sigma_0(\mathbf{R})$ is defined by equating the energy shift of the perturbed system to the integral of the self-energy weighted by the probability of finding the system in the initial state:

$$\Delta E_0=\int d\mathbf{R}\,\phi_0^*(R)\Sigma_0(\mathbf{R})\phi_0(\mathbf{R})\,. \tag{6}$$

As shown previously[4] this self-energy can be generalized to all orders of perturbation theory, but for the problem at hand we will be interested in the energy shift to second order, given by

$$\Delta E_0=\sum_j|(j|H'|0)|^2/(E_0-E_j)\,, \tag{7}$$

which leads to a spatially dependent self-energy of the form

$$\Sigma_0^a(\mathbf{R})=\sum_j\frac{\phi_j(\mathbf{R})}{\phi_0(\mathbf{R})}\frac{\langle 00|H'|n_jl_j\rangle(j|H'|0)}{E_0-E_j}\,. \tag{8}$$

The matrix elements represented by angular brackets ⟨ ⟩ are taken with respect to atomic states only, while those represented by ( ) include also the state of relative motion, as shown in Eq. (1). After Fourier expansion of the perturbation (4), 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

$$\Sigma_0^a(R)=\frac{1}{2\pi^2}\sum_l\sum_n\langle 00|H'|ln\rangle\langle nl|\tilde{I}|00\rangle\,, \tag{9}$$

where

$$\tilde{I}=\sum_{i=1}^{4}(-1)^i\int(d\mathbf{Q}/Q^2)e^{i\mathbf{Q}\cdot(\mathbf{R}-\mathbf{R}_i)}\times\{\epsilon_l+\epsilon_n+[Q_0^2-(\mathbf{Q}_0+\mathbf{Q})^2]/2\mu\}^{-1}\,. \tag{10}$$

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[1] are recovered. Evaluating the operator of Eq. (10) for a general relative momentum $\mathbf{Q}_0$ of the unperturbed system is straightforward but leads to complicated forms beyond the scope of this letter. However, many features of the general problem can be illustrated by looking at the special limiting case of two atoms with no relative motion, $\mathbf{Q}_0=0$. Then all integrals can be readily evaluated to give the self-energy in the form

$$\Sigma_0^a(\mathbf{R})=-\sum_l\sum_n\frac{1}{|\epsilon_l+\epsilon_n|}\langle 00|H'|ln\rangle\left\langle ln\left|H'-\sum_{i=1}^{4}(-1)^i\frac{e^{-a|\mathbf{R}-\mathbf{R}_i|}}{|\mathbf{R}-\mathbf{R}_1|}\right|00\right\rangle\,, \tag{11}$$

where $a^2=2\mu|\epsilon_l+\epsilon_n|$. The terms exponentially decreasing in R in the second matrix element of (11) are due to the quantum-mechanical recoil; specifically, they arise from the term in Q^2 in the denominator of Eq. (10). For large R Eq. (11) becomes the familiar London form of the $1/R^6$ van der Waals potential. Further discussion of Eq. (11) 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 $\Sigma_0^a(R)$ is finite as $R\rightarrow 0$, whereas if one makes the expansion for a point dipole the short-range self-energy approaches the form

$$\Sigma_0^a(R)\rightarrow(2\mu/9R^4)\langle 0|\mathbf{r}_1^2|0\rangle\langle 0|\mathbf{r}_2^2|0\rangle,\quad aR\rightarrow 0\,. \tag{12}$$

A similar comparison has been noted in the somewhat related case of an atom interacting with the collective electronic excitations of a solid surface.[7]

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

$$H^q=\sum_{i=1}^{2}(-1)^i|\mathbf{R}-\mathbf{L}_i|^{-1}\,, \tag{13}$$

with

$$\mathbf{L}_1=-\mathbf{r}/(m+1),\quad \mathbf{L}_2=m\mathbf{r}/(m+1)\,, \tag{14}$$

where $\mathbf{r}$ is the atomic displacement operator and $\mathbf{R}$ is the vector joining the charge to the center of mass of the atom. The self-energy is again defined by Eq. (8) and can be put in a form similar to the atomic case of Eq. (9)

$$\Sigma_0^q(\mathbf{R})=\frac{1}{2\pi^2}\sum_n\langle 0|H^q|n\rangle\langle n|I'|0\rangle\,, \tag{15}$$

with the atomic operator I' given by

$$I'=\int(d\mathbf{Q}/Q^2)e^{i\mathbf{Q}\cdot\mathbf{R}}\sum_{i=1}^{2}\exp(-i\mathbf{Q}\cdot\mathbf{L}_i)\times[\epsilon_n-(2\mathbf{Q}\cdot\mathbf{Q}_0-Q^2)/2\mu_q]^{-1}\,, \tag{16}$$

where the reduced mass in this case is

$$\mu_q = (m+1)/(m+2) \; . \tag{17}$$

Again the integrals in Eq. (16) can be carried out for all values of $\mathbf{Q}_0$ but this leads to some lengthy and cumbersome equations.[8] The case of zero relative motion $\mathbf{Q}_0=0$ leads to a simple expression in compact form similar to Eq. (11):

$$\Sigma_0^q(\mathbf{R}) = -\sum_n \frac{1}{|\epsilon_n|}\langle 0|H^q|n\rangle \times \left\langle n \left| H^q - \sum_{i=1}^{2}(-1)^i \frac{e^{-b|\mathbf{R}-\mathbf{L}_i|}}{|\mathbf{R}-\mathbf{L}_i|} \right| 0 \right\rangle \; , \tag{18}$$

where $b^2 = 2\mu_q|\epsilon_n|$. As was pointed out for the case of Eq. (11), when Eq. (18) is developed in an expansion in large values of the separation distance R, one recovers all previously obtained results for the multipole series,[2] beginning with the long-range polarization potential which behaves as $1/R^4$. However, Eq. (18) 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 $R \rightarrow 0$ is zero. On the other hand, if the mass m is very large we have

$$\Sigma_0^q(0) \rightarrow -m, \quad m \rightarrow \infty \; . \tag{19}$$

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

By way of contrast, if we look at only the contribution of a point dipole, the interaction self-energy saturates to a $1/R^2$ form but is still divergent.[2,5]

$$\Sigma_0^q(R) \rightarrow -\frac{\mu_q}{3R^2}\langle 0|\mathbf{r}^2|0\rangle \; . \tag{20}$$

Another interesting point arises for the positronium-charge system. When all the masses are of unit magnitude, the self-energy involves matrix elements of the form

$$\langle i \,|\, |\mathbf{R}+\mathbf{r}/2|^{-1} - |\mathbf{R}-\mathbf{r}/2|^{-1} \,|\, n \rangle \tag{21}$$

and clearly all even terms in the multipole expansion will vanish. A similar effect occurs in the interaction of two positronium atoms[9,10] as can be shown with Eq. (11).

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. These closed forms also clearly show that when the atoms are positronium, terms of even parity in the multipole series are not present.

Since these calculations were carried out without imposing the Born-Oppenheimer approximation, the nonadiabatic 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. This finite interaction energy is a reflection of the fact that in a real quantum-mechanical atom of finite mass both the nucleus and the electron must be viewed as "charge clouds" and the self-energy at that separation distance is just the interaction energy of the corresponding overlapping charge distributions.

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