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The integration of multiplet van der Waals interactions

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Abstract. The integration method for many-particle van der Waals interactions of general order, which was found useful in Drude model calculations, can be successfully used also in purely quantum mechanical investigations. The quantum mechanical perturbation series of the dispersion energy is shown not to contain any poles even if the unperturbed electron states are degenerate. It is factorized by means of a linear integral transformation, and subsequently integrated by combining concurrent interactions into effective matrix elements (Green's functions).

1. Introduction

Recently, an analytical summation of van der Waals interactions between all multiplets of atoms in a macroscopic ensemble was reported (Bade 1957, Lucas 1967, 1968, Nijboer and Renne 1967, 1968, Langbein 1971a). It enables a representation of the dispersion energy between macroscopic bodies by their macroscopic reaction fields (Langbein 1969, 1971a,b). The basis of the calculation is the Drude model of dispersion, which replaces each atom by a number of harmonic dipole oscillators. Each dipole exhibits its quantum mechanical zero-point energy. The change of the characteristic frequencies via the interaction with all other dipoles causes a decrease of the total zero-point energy, that is, an attractive dispersion energy.

The determination of the perturbed dipole frequencies and the summation of multiplet interactions involve the solution of a linear secular problem and the introduction of a diagram technique. These steps and the generality of the final energy expression (Nijboer and Renne 1968, Langbein 1969, 1971b) suggest an easy extension of the procedure according to the Drude model to quantum mechanical methods. It is the aim of this paper to show that a similar diagram technique and summation of multiplet terms is also applicable to the calculation of the total energy of arbitrary systems of interacting non-overlapping electron states.

The proposed method enables a general summation of multiplet interactions in a purely quantum mechanical treatment of the dispersion energy (London 1930, 1937, Margenau 1939, Axilrod 1951), and also eliminates the restriction to include only interactions via electric dipole fields. The final energy expression turns out to be closely related to that resulting from many-particle Green's function techniques, and may be also applied to electrons interacting via phonons, i.e. to the problem of superconductivity.

2. Perturbation theory

Let us consider an orthonormal set of unperturbed one-electron states $|i\rangle$, which interact via the Hamiltonian H . Then, for the coefficients a_{ij} of the perturbed one-electron states $\psi_i = \sum a_{ij}|j\rangle$ we obtain the secular equations

$$(H_{ii} - E)a_{ii} + \sum_{j \neq i} H_{ij}a_{ij} = 0 \quad (1)$$

($i = 1, 2, \dots$). According to perturbation theory, the perturbed eigenvalues are given by

$$E_i = H_{ii} + \sum_{j \neq i} \frac{H_{ij}H_{ji}}{E_i - H_{jj}} + \sum_{j,k \neq i} \frac{H_{ij}H_{jk}H_{ki}}{(E_i - H_{jj})(E_i - H_{kk})} + \dots \quad (2)$$

The energy gain of the electron system due to the interaction via H is the sum over the energy gain $E_i - H_{ii}$ of all occupied states $|i\rangle$, and we are interested in

$$\Delta E = \sum_{i \in a} (E_i - H_{ii}) \quad (3)$$

where $i \in a$ denotes that $|i\rangle$ is occupied, while $i \in b$ means that state $|i\rangle$ is unoccupied. By inserting (2) into (3) we obtain

$$\Delta E = \Delta_2 E + \Delta_3 E + \Delta_4 E + \dots \quad (4)$$

where

$$\Delta_2 E = \sum_{i \in a; j \neq i} \frac{H_{ij}H_{ji}}{H_{ii} - H_{jj}} \quad (5)$$

$$\Delta_3 E = \sum_{i \in a; j, k \neq i} \frac{H_{ij}H_{jk}H_{ki}}{(H_{ii} - H_{jj})(H_{ii} - H_{kk})} \quad (6)$$

$$\begin{aligned} \Delta_4 E = & \sum_{i \in a; j, k, l \neq i} \frac{H_{ij}H_{jk}H_{kl}H_{li}}{(H_{ii} - H_{jj})(H_{ii} - H_{kk})(H_{ii} - H_{ll})} \\ & - \sum_{i \in a; j, k \neq i} \frac{H_{ij}H_{ji}H_{ik}H_{ki}}{(H_{ii} - H_{jj})^2(H_{ii} - H_{kk})} \end{aligned} \quad (7)$$

The second sum in (7) results from the iterative substitution of E_i into the denominators on the right-hand side of (2). A critical condition for the convergence of perturbation series like (2) is that the unperturbed eigenvalues H_{ii} must be non-degenerate. The iterative substitution of E_i into the denominators of (2) causes several of them to vanish otherwise. We are left with poles of the individual terms. This does not apply, however, to the total energy gain ΔE . All poles arising in the individual terms cancel mutually as a consequence of the conservation law for level centres.

In order to prove this theorem we start by dissecting the sum over i in (5) into two sums extending over $j \in a$ and $j \in b$. We show the first of these sums to vanish by interchanging the summation indices i and j , which both cover all occupied states, $i, j \in a$. This leaves us with the second sum

$$\Delta_2 E = - \sum_{i \in a; j \in b} \frac{H_{ij}H_{ji}}{H_{jj} - H_{ii}} \quad (8)$$

A similar dissection of the sums over j, k, l in (6), (7) and a subsequent interchange of summation indices yields

$$\Delta_3 E = - \sum_{i, j \in a; k \in b} \frac{H_{ij}H_{jk}H_{ki}}{(H_{kk} - H_{ii})(H_{kk} - H_{jj})} + \sum_{i \in a; j, k \in b} \frac{H_{ij}H_{jk}H_{ki}}{(H_{jj} - H_{ii})(H_{kk} - H_{ii})} \quad (9)$$

$$\begin{aligned}
 \Delta_4 E = & - \sum_{i,j,k \in a; l \in b} \frac{H_{ij} H_{jk} H_{kl} H_{li}}{(H_{ll} - H_{ii})(H_{ll} - H_{jj})(H_{ll} - H_{kk})} \\
 & - \sum_{i \in a; j,k,l \in b} \frac{H_{ij} H_{jk} H_{kl} H_{li}}{(H_{jj} - H_{ii})(H_{kk} - H_{ii})(H_{ll} - H_{ii})} \\
 & + \sum_{i,j \in a; k,l \in b} \frac{H_{ij} H_{jk} H_{kl} H_{li}}{(H_{kk} - H_{ii})(H_{ll} - H_{jj})} \left(\frac{1}{H_{ll} - H_{ii}} + \frac{1}{H_{kk} - H_{jj}} \right) \\
 & + \sum_{i,k \in a; j,l \in b} \frac{H_{ij} H_{jk} H_{kl} H_{li}}{(H_{jj} - H_{ii})(H_{jj} - H_{kk})(H_{ll} - H_{kk})}. \tag{10}
 \end{aligned}$$

We now have summations extending either over occupied states or over unoccupied states so that no poles arise if the electrons occupy the unperturbed states according to Fermi statistics. The unperturbed states $|i\rangle$ are assumed to be occupied for H_{ii} smaller than the Fermi energy ζ , and to be unoccupied for H_{ii} larger than the Fermi energy ζ . This occupation status is taken to be adiabatically maintained by the perturbed level system E_i .

Consequently, we find the second-order contribution $\Delta_2 E$ to be negative owing to $|H_{ij}|^2 > 0$ and $H_{jj} > \zeta > H_{ii}$. The total electron energy decreases in second order of perturbation, independent of the special form of the interaction Hamiltonian H . The sign of the third and fourth order contributions $\Delta_3 E$ and $\Delta_4 E$ is not fixed in the same manner; the denominators in (9), (10) are all chosen to be positive.

A similar cancellation of poles in ΔE may be proved in general order of perturbation.

3. Factorization

In treating van der Waals attraction by means of the Drude model, the cancellation of poles in the perturbation series for ΔE is one essential simplification. A second is the introduction of a linear integral transformation, which factorizes the frequency term adjoined to a multiplet i, j, k, \dots of dipoles. This factorization enables the summation of the individual dipole contributions to atomic polarizabilities, and the integration of the atomic induction fields to macroscopic reaction fields.

In view of the obvious simplifications introduced by the integral transformation, we now look for an equivalent transformation of the quantum mechanical approach. Is it possible to find a linear integral operator $O(\xi)$ which, applied to a factorized representation $f(\xi, H_{ii})f(\xi, H_{jj})f(\xi, H_{kk})\dots$ of the sequence i, j, k, \dots of states, yields the denominators given in (8) to (10), and also the correct higher order terms?

A detailed examination of equations (8) to (10) reveals the conditions

$$\begin{aligned}
 O(\xi) f(\xi, H_{ii}) f(\xi, H_{jj}) f(\xi, H_{kk}) \dots \\
 = 1/(H_{ii} - H_{jj})(H_{ii} - H_{kk}) \dots & \quad \text{for } i \in a; j, k, \dots \in b \tag{11}
 \end{aligned}$$

$$= -1/(H_{ii} - H_{jj})(H_{ii} - H_{kk}) \dots \quad \text{for } i \in b; j, k, \dots \in a \tag{12}$$

$$= \{1/(H_{ii} - H_{kk}) \dots - 1/(H_{jj} - H_{kk})\} / (H_{ii} - H_{jj}) \quad \text{for } i, j \in a; k, \dots \in b. \tag{13}$$

According to an investigation of the higher-order terms, equation (13) turns out to be a special case of the general condition

$$\begin{aligned} &O(\xi) f(\xi, H_{ii}) f(\xi, H_{jj}) f(\xi, H_{kk}) \dots \\ &= O(\xi) \frac{f(\xi, H_{ii}) - f(\xi, H_{jj})}{H_{ii} - H_{jj}} f(\xi, H_{kk}) \dots \end{aligned} \tag{14}$$

for $i, j \in a$ or $i, j \in b$. Condition (14) yields the functional relation

$$f(\xi, H_{ii}) f(\xi, H_{jj}) = \frac{f(\xi, H_{ii}) - f(\xi, H_{jj})}{H_{ii} - H_{jj}} \tag{15}$$

which can be satisfied by

$$f(\xi, H_{ii}) = \frac{1}{G(\xi) - H_{ii}} \tag{16}$$

with $G(\xi)$ being an arbitrary function of ξ . Having fixed the functional form of $f(\xi, H_{ii})$ from conditions (13) and (14), we determine the explicit form of the integral operator $O(\xi)$ by satisfying conditions (12) and (13). With respect to (14) it proves sufficient to satisfy these conditions for $i \in a, j \in b$. On the basis of

$$\begin{aligned} &= 0 \quad \text{for } H_{ii}, H_{jj} < \zeta \\ \frac{1}{2\pi i} \int_{-1^\infty}^{1^\infty} d\xi \frac{1}{(\xi - H_{ii})(\xi - H_{jj})} &= \frac{1}{H_{ii} - H_{jj}} \quad \text{for } H_{ii} < \zeta < H_{jj} \\ &= 0 \quad \text{for } \zeta < H_{ii}, H_{jj} \end{aligned} \tag{17}$$

where the path of integration crosses the real ξ axis at the Fermi energy ζ , we put

$$O(\xi) = \frac{1}{2\pi i} \int_{-1^\infty}^{1^\infty} d\xi \tag{18}$$

and

$$f(\xi, H_{ii}) = \frac{1}{\xi - H_{ii}}. \tag{19}$$

Hence,

$$\begin{aligned} \Delta E = \frac{1}{2\pi i} \int_{-1^\infty}^{1^\infty} d\xi \left\{ \frac{1}{2} \sum_{i,j} \frac{H_{ij} H_{ji}}{(\xi - H_{ii})(\xi - H_{jj})} + \frac{1}{3} \sum_{i,j,k} \frac{H_{ij} H_{jk} H_{ki}}{(\xi - H_{ii})(\xi - H_{jj})(\xi - H_{kk})} \right. \\ \left. + \frac{1}{4} \sum_{i,j,k,l} \frac{H_{ij} H_{jk} H_{kl} H_{li}}{(\xi - H_{ii})(\xi - H_{jj})(\xi - H_{kk})(\xi - H_{ll})} + \dots \right\}. \end{aligned} \tag{20}$$

The sums over i, j, k, \dots in (20) include all electron states. In order to compensate for the fact that all summations are now equivalent, we multiplied the terms of order n by $1/n$. All terms in (20), which contain only occupied or only unoccupied states, vanish after integration over ξ .

4. Applications

The factorized representation (20) of the total interaction energy enables several simplifications and extensions:

(i) If there are several states $k \in A$, which do not directly interact with each other, we find their joint contribution to the interaction between other states $i, j \notin A$ to be

$$H_{ij}^{\text{int}} = \sum_{k \in A} \frac{H_{ik} H_{kj}}{\xi - H_{kk}}. \quad (21)$$

A summation of this type is the fusion of the individual dipole contributions to atomic polarizabilities in the Drude model formalism of van der Waals attraction (Langbein 1970a).

(ii) Let us consider two groups of states A and B, which interact strongly if they belong to the same group, and only weakly when belonging to different groups. It is then convenient to summarize first the interactions within the same group, and to introduce effective matrix elements

$$H_{ij}^{\text{eff}} = H_{ij} + \sum_{k \in A} \frac{H_{ik} H_{kj}}{\xi - H_{kk}} + \sum_{k, l \in A} \frac{H_{ik} H_{kl} H_{li}}{(\xi - H_{kk})(\xi - H_{ll})} + \dots \quad (22)$$

for the interactions between states belonging to different groups, $i \in A, j \in B$. Using (22) the total interaction energy ΔE_{AB} between groups A and B can be written in the form

$$\Delta E_{AB} = \frac{1}{2\pi i} \int_{-i\infty}^{i\infty} d\xi \left\{ \sum_{i \in A} \sum_{j \in B} \frac{H_{ij}^{\text{eff}} H_{ji}^{\text{eff}}}{(\xi - H_{ii})(\xi - H_{jj})} + \frac{1}{2} \sum_{i, k \in A} \sum_{j, l \in B} \frac{H_{ij}^{\text{eff}} H_{jk}^{\text{eff}} H_{kl}^{\text{eff}} H_{li}^{\text{eff}}}{(\xi - H_{ii})(\xi - H_{jj})(\xi - H_{kk})(\xi - H_{ll})} + \dots \right\}. \quad (23)$$

H_{ii}^{eff} is closely related to the Green's function $G(i, j)$ corresponding to states $|i\rangle$ and $|j\rangle$. We obtain

$$G(i, j) \equiv \left\langle i \left| \frac{1}{\xi - H} \right| j \right\rangle = \frac{H_{ij}^{\text{eff}}}{(\xi - H_{ii})(\xi - H_{jj})}. \quad (24)$$

The analogue to H_{ij}^{eff} in the Drude model formalism of van der Waals attraction between solids A and B is the screened field T_{ij}^{scr} of dipole i in A at position j in B.

(iii) In the above investigations we assumed for simplicity that the states $|i\rangle$ be one-electron states. However, the procedure is also applicable if the states $|i\rangle$ represent the ground and excited states of distinct groups of electrons, as for instance of electrons localized at the same molecule. Though the superiority of such a many-electron formalism cannot be questioned, this method does not yield additional information on the van der Waals attraction for lack of experimental data.

(iv) An application of the above formalism to superconductivity, where the electron pair states and hole pair states can be assumed to form groups A and B as discussed in (ii) will be reported in a subsequent paper.

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