The van der Waals interaction¹ D. E. Soper² University of Oregon 20 April 2012

The van der Waals interaction is discussed in Chapter 5 of J. J. Sakurai, *Modern Quantum Mechanics*. Here I take a look at it in a little more depth. It provides a nice application of perturbation theory.

1 Two atoms

We consider two atoms A and B.

Atom A has a center of mass position \vec{R}_A and constituents at positions $\vec{r}_a + \vec{R}_A$. That is, \vec{r}_a is the difference between the constituent position and the center of mass position. The constituents have charges e_a and masses m_a . The indices a are in a set that we will call A. One of the constituents is the nucleus. The relative position \vec{r}_a for the nucleus is very small (the nucleus is close to the center of mass), so we can take \vec{r}_a for the nucleus to be zero. If the atom is neutral, then $\sum e_a = 0$. We will be most interested in that case, but we will also consider the possibility of an ion, for which the total charge is not zero.

Atom B has a center of mass position \vec{R}_B and constituents at positions $\vec{r}_b + \vec{R}_B$. The constituents have charges e_b and masses m_b . The indices b are in a set that we will call B.

The hamiltonian is $H = H_A + H_B + V$ where H_A is the hamiltonian for atom A by itself,

$$H_A = \sum_{a \in A} \frac{\vec{p}_a^2}{2m_a} + \frac{1}{2} \sum_{a \in A} \sum_{\substack{a' \in A \\ a' \neq a}} \frac{e_a e_{a'}}{|\vec{r}_a - \vec{r}_{a'}|} \quad , \tag{1}$$

 H_B is the hamiltonian for atom B by itself,

$$H_B = \sum_{a \in B} \frac{\vec{p}_b^2}{2m_b} + \frac{1}{2} \sum_{b \in B} \sum_{\substack{b' \in B \\ b' \neq b}} \frac{e_b e_{b'}}{|\vec{r_b} - \vec{r_{b'}}|} \quad , \tag{2}$$

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and V is the interaction between the two atoms,

$$V = \sum_{a \in A} \sum_{b \in B} \frac{e_a e_b}{|R\vec{n} + \vec{r_a} - \vec{r_b}|} \quad , \tag{3}$$

where

$$R = |\vec{R}_a - \vec{R}_b| \tag{4}$$

and \vec{n} is a unit vector in the direction of $\vec{R}_a - \vec{R}_b$

$$R\,\vec{n} = \vec{R}_a - \vec{R}_b \quad . \tag{5}$$

We would like to analyze this situation in the Born-Openheimer approximation. The atoms exert a force on each other. We think of the atoms as moving slowly and the electrons in each atom as moving quickly. Then as the atoms move, the electron orbits in each atom adjust very quickly to the separation $R\vec{n}$ between the atoms. The atom energy levels thus slowly change. This shift in energy then constitutes an effective potential $V_{\rm BO}(R)$ between the atoms. This effective potential is, approximately, a replacement for the exact V.

The Born-Openheimer approximation is pretty intuitive, but we will not explore it further in these notes. Rather, our task here is to determine how $V_{BO}(R)$ depends on the separation R. We assume that both atoms are in their ground states and that the separation R is large compared to the sizes of the atoms. For this purpose, we take the separation $R\vec{n}$ to be fixed.

2 The interaction for large separation

Having set up the problem, we now need to work out what V looks like when the separation $R \vec{n}$ is large compared to the intra-atomic separations $\vec{r_a}$ and $\vec{r_b}$. That is, we ask how

$$\Phi(R\vec{n} + \vec{\Delta}) = \frac{1}{|R\vec{n} + \vec{\Delta}|} = \frac{1}{R} \frac{1}{[1 + 2\vec{n} \cdot \vec{\Delta}/R + \vec{\Delta}^2/R^2]^{1/2}}$$
(6)

behaves when $R \gg |\vec{\Delta}|$. Using

$$\frac{1}{\sqrt{1+\epsilon}} = 1 - \frac{1}{2}\epsilon + \frac{3}{8}\epsilon^2 + \cdots , \qquad (7)$$

we have

$$\Phi(R\vec{n}+\vec{\Delta}) = \frac{1}{R} \left[1 - \frac{1}{2} (2\vec{n}\cdot\vec{\Delta}/R + \vec{\Delta}^2/R^2) + \frac{3}{8} (2\vec{n}\cdot\vec{\Delta}/R)^2 + \cdots \right] \quad . \tag{8}$$

That is,

$$\Phi(R\vec{n} + \vec{\Delta}) = \frac{1}{R} \left[1 - \frac{1}{R}\vec{n} \cdot \vec{\Delta} - \frac{1}{2R^2} \left[\vec{\Delta}^2 - 3(\vec{n} \cdot \vec{\Delta})^2 \right] + \cdots \right] \quad . \tag{9}$$

This has the form

$$\Phi(R\vec{n}+\vec{\Delta}) = \frac{1}{R} \left[1 - \frac{1}{R} P_1(\vec{n})^i \Delta^i - \frac{1}{2R^2} P_2(\vec{n})^{ij} \Delta^i \Delta^j + \cdots \right] \quad , \tag{10}$$

where

$$P_1(\vec{n})^i = n^i ,$$

$$P_2(\vec{n})^{ij} = \delta^{ij} - 3n^i n^j .$$
(11)

This series goes on. The next term has the form const. $\times P_3(\vec{n})^{ijk} \Delta^i \Delta^j \Delta^k / R^3$. We note that P_2^{ij} is symmetric under interchange of i, j and is traceless: $P_2^{ij} \delta_{ij} = 0$. The higher order tensors P_J are also completely symmetric and traceless in all pairs of indices. As we will see, this expansion is related to multipole moments.

We can use this to expand our interaction V, using $Q_A = \sum_a e_a$ and $Q_B = \sum_b e_b$,

$$V = \sum_{a \in A} \sum_{b \in B} \frac{e_a e_b}{|R\vec{n} + \vec{r_a} - \vec{r_b}|}$$

$$= \frac{1}{R} \sum_{a \in A} \sum_{b \in B} e_a e_b - \frac{1}{R^2} \sum_{a \in A} \sum_{b \in B} e_a e_b P_1(\vec{n})^i (r_a^i - r_b^i)$$

$$- \frac{1}{2R^3} \sum_{a \in A} \sum_{b \in B} e_a e_b P_2(\vec{n})^{ij} (r_a^i - r_b^i) (r_a^j - r_b^j) + \cdots$$

$$= \frac{Q_A Q_B}{R} + \frac{Q_A}{R^2} \sum_{b \in B} e_b P_1(\vec{n})^i r_b^i - \frac{Q_B}{R^2} \sum_{a \in A} e_a P_1(\vec{n})^i r_a^i$$

$$- \frac{Q_A}{2R^3} \sum_{b \in B} e_b P_2(\vec{n})^{ij} r_b^i r_b^j - \frac{Q_B}{2R^3} \sum_{a \in A} e_a P_2(\vec{n})^{ij} r_a^i r_a^j$$

$$+ \frac{1}{R^3} \sum_{a \in A} \sum_{b \in B} e_a e_b P_2(\vec{n})^{ij} r_a^i r_b^j + \cdots$$

(12)

3 First order perturbation theory

We can evaluate the interaction energy in first order perturbation theory by simply taking the expectation value $\langle V \rangle$ of V in the ground states of the two atoms.

The biggest term is $Q_A Q_B / R$. This is the electrostatic attraction or repulsion between the two atoms. If Q_A and Q_B are nonzero, this term is larger than any of the other terms (in an expansion in powers of (atom size)/R).

We will mostly be interested in two neutral atoms, $Q_A = Q_B = 0$. However, first, it is interesting to consider the case that Q_A is zero but Q_B is not. Then what contribution is biggest for large R? Then there is a $1/R^2$ term proportional to

$$P_1(\vec{n})^i \left\langle \sum_{a \in A} e_a r_a^i \right\rangle \quad . \tag{13}$$

This term describes the interaction of the electric dipole moment of atom A with the field from atom B. However the expectation value in the ground state of the electric dipole moment of atom A must vanish. If the total angular momentum of atom A is zero, then this statement follows from rotational invariance. Even if the total angular momentum of atom A is not zero, parity invariance prevents the dipole moment from being non-zero as long as the ground state is a parity eigenstate. Furthermore, the ground state must be a parity eigenstate as long as it is not degenerate. Thus we can safely rule out a non-vanishing $1/R^2$ term. There is a $1/R^3$ term proportional to

$$P_2(\vec{n})^{ij} \left\langle \sum_{a \in A} e_a r_a^j r_a^j \right\rangle \quad . \tag{14}$$

This term describes the interaction of the electric quadrupole moment of atom A with the field from atom B. If atom A has angular momentum zero, then rotational invariance gives

$$\left\langle \sum_{a \in A} e_a r_a^j r_a^j \right\rangle \propto \delta^{ij} \quad . \tag{15}$$

But $P_2(\vec{n})^{ij}\delta_{ij} = 0$, so we get a contribution zero.³ If atom A has, say, angular momentum 1, then I think that it can have a quadrupole moment and we can get a non-zero contribution.

³Actually, we also get a zero contribution if the total angular momentum is 1/2, but the

There is another $1/R^3$ contribution, proportional to

$$P_2(\vec{n})^{ij} \left\langle \sum_{a \in A} e_a r_a^j \right\rangle_A \left\langle \sum_{b \in B} e_b r_b^j \right\rangle_B \quad . \tag{16}$$

This term is present even if the total charge of both atoms vanish. This contribution vanishes because the expectation values of the dipole moments vanish.

At the order $1/R^4$, we get contributions like

$$P_3(\vec{n})^{ijk} \left\langle \sum_{a \in A} e_a r_a^j r_a^j \right\rangle_A \left\langle \sum_{b \in B} e_b r_b^k \right\rangle_B \quad . \tag{17}$$

At the order $1/R^5$, we get a term proportional to

$$P_4(\vec{n})^{ijkl} \left\langle \sum_{a \in A} e_a r_a^j r_a^j \right\rangle_A \left\langle \sum_{b \in B} e_b r_b^k r_b^l \right\rangle_B \quad . \tag{18}$$

Terms like this are there even if the total charge of both atoms vanish. The dipole moment factor

$$\left\langle \sum_{b \in B} e_b r_b^k \right\rangle_B \tag{19}$$

will vanish by the parity argument given previously. For the $1/R^5$ term in Eq. (18), we could possibly have a non-zero contribution. However, if the angular momenta of the ground states vanish, then Eq. (15) applies and the contribution vanishes because $P_4(\vec{n})^{ijkl}\delta_{kl} = 0$.

In fact, we see that there is a remarkable consequence if the ground states have angular momentum zero: all of the contributions to $\langle V \rangle$ vanish. This means that we should look at second order perturbation theory.

4 Second order perturbation theory

We have seen that if the atoms have zero charge, are in their ground state, and have angular momentum zero, $\langle V \rangle = 0$ and we need to go to second

argument is a little more subtle. $\sum e_a P_2(\vec{n})^{ij} r_a^j r_a^j$ is an angular momentum 2 operator. If we combine angular momentum 2 with angular momentum 1/2 for the ket state, we can angular momentum 3/2 or 5/2, but we cannot get angular momentum 1/2 to match the bra state.

order perturbation theory to look for the energy shift. With $Q_A = Q_B = 0$, the interaction V is

$$V = \frac{1}{R^3} \sum_{a \in A} \sum_{b \in B} e_a e_b P_2(\vec{n})^{ij} r_a^i r_b^j + \cdots \quad .$$
 (20)

The corresponding second order energy shift is

$$\Delta = \frac{1}{R^6} \sum_{a,a' \in A} e_a e_{a'} \sum_{K \neq 0} \langle 0, A | r_{a'}^l | K, A \rangle \langle K, A | r_a^j | 0, A \rangle$$

$$\times \sum_{b,b' \in B} e_b e_{b'} \sum_{L \neq 0} \langle 0, B | r_{b'}^k | L, B \rangle \langle L, B | r_b^i | 0, B \rangle$$

$$\times \frac{P_2(\vec{n})^{ij} P_2(\vec{n})^{kl}}{E_0^{(A)} + E_0^{(B)} - E_K^{(A)} - E_L^{(B)}} .$$
(21)

Here $|0, A\rangle$ is the ground state for atom A and the states $|K, A\rangle$ are the states other than the ground state. An analogous notation applies for atom B. The sums over states of the atoms, as dictated by the projection operator Q, includes all states $\{K, L\}$ except the state $\{0, 0\}$ consisting of both atoms in their ground states. In our application, neither $\{0, L\}$ for $L \neq 0$ nor $\{K, 0\}$ for $K \neq 0$ contribute because the dipole moment operator has vanishing matrix element between $\langle 0 |$ and $|0 \rangle$.

We can think of this energy shift as representing a dipole-dipole interaction, where the two atoms induce dipole moments in each other.

It is not so easy to find approximations for the matrix elements and sums here. However, even without doing that, we learn something interesting: neutral atoms will experience a $1/R^6$ potential at large separations. This is known as the van der Waals potential.

Notice something else. We get a $1/R^6$ potential. If we used terms in V with more powers of 1/R or if we used higher order in perturbation theory, we would get additional contributions, which would be proportional to $1/R^n$ with n > 6. This tells us that if we expand $V_{\rm BO}(R)$ in powers of (atom size)/R, the first contribution is proportional to $1/R^6$ and that the result in Eq. (21) gives the $1/R^6$ contribution exactly.