## Intermolecular van der Waals Interactions

Our goal is to calculate the interaction energy, $U(R)$, between two charge distributions located at a large distance from each other, as illustrated in Figure 1. As is well known, for two neutral charge distribution (i.e., $\left.Q=Q^{\prime}=0\right) \quad U(R)=-C / \mathrm{R}^{6}$. The van der Waals constant $C$ depends on the molecular characteristics of the two charge distributions, and if one or both of them possess a permanent dipole moment it depends on the temperature as well. Our main goal is to derive an explicit expression for $C$ for both polar and non-polar molecules, but we shall also consider the interaction energies between two ions (in which case $Q \neq 0, Q^{\prime} \neq 0$ ) or an ion and a molecule (i.e., $Q \neq 0, Q^{\prime}=0$ or $Q=0, Q^{\prime} \neq 0$ ). To these ends we will need to carry out temperature and/or quantum mechanical averages of $V$, the electrostatic (Coulomb) interaction energy between the two charge distributions. That is $U(R)=\langle V\rangle$.

Using cgs (electrostatic) units, and assuming that the two charge distributions are in vacuum, we have

$$
\begin{equation*}
V=\sum_{i, j} \frac{q_{i} q_{j}^{\prime}}{R_{i j}}=\sum_{i, j} \frac{q_{i} q_{j}^{\prime}}{\left[\left(X-x_{i}+x_{j}^{\prime}\right)^{2}+\left(Y-y_{i}+y_{j}^{\prime}\right)^{2}+\left(Z-z_{i}+z_{j}^{\prime}\right)^{2}\right]^{1 / 2}} \tag{1}
\end{equation*}
$$

In the second equality we have used the explicit expression for the $R_{i j}$ 's, the distances between charges $q_{i}$ of one charge distribution (the one on the left in Figure 1) and charge $q_{j}^{\prime}$ of the other,

$$
\begin{equation*}
R_{i, j}=\sqrt{\left[\left(X-x_{i}+x_{j}^{\prime}\right)^{2}+\left(Y-y_{i}+y_{j}^{\prime}\right)^{2}+\left(Z-z_{i}+z_{j}^{\prime}\right)^{2}\right]} \tag{2}
\end{equation*}
$$

Here $X, Y, Z$ are the Cartesian coordinated of the vector $\vec{R}$ - an arbitrary vector connecting two reference points one in the first charge distribution and another on the second. The magnitude of $\vec{R}$ is $|\vec{R}|=R=\sqrt{\left[X^{2}+Y^{2}+Z^{2}\right]}$. Similarly, $x_{i}$ is the $x$ component of the vector $\vec{r}_{i}$ which measures the position of charge $q_{i}$ from the reference point of the left charge distribution, etc.

Figure 1


## The multipole expansion

We are interested in cases where all $r_{i}$ and $r_{j}^{\prime}$ are much smaller than $R$. We can thus suffice in the low order terms of the Taylor expansion series of $V$ around $R$, that is,

$$
\begin{align*}
V= & V\left(\vec{R},\left\{\vec{r}_{i}\right\},\left\{\vec{r}_{j}^{\prime}\right\}\right)=V(R)+\sum_{i, j}\left(\frac{\partial V}{\partial \vec{r}_{i}} \cdot \vec{r}_{i}+\frac{\partial V}{\partial \vec{r}_{j}^{\prime}} \cdot \partial \vec{r}_{j}^{\prime}\right) \\
& +\frac{1}{2}\left\{\sum_{i, k} \vec{r}_{i} \cdot \frac{\partial^{2} V}{\partial \vec{r}_{i} \partial \vec{r}_{k}} \bullet \vec{r}_{k}+\sum_{j, l} \vec{r}_{j}^{\prime} \cdot \frac{\partial^{2} V}{\partial \vec{r}_{j}^{\prime} \partial \vec{r}_{l}^{\prime}} \cdot \vec{r}_{l}^{\prime}+\sum_{i, k} \vec{r}_{i} \cdot \frac{\partial^{2} V}{\partial \vec{r}_{i} \partial \vec{r}_{k}^{\prime}} \bullet \vec{r}_{k}^{\prime}\right\}+\cdots \tag{3}
\end{align*}
$$

with all derivatives evaluated at $R_{i j}=R$ (for all $i, j$ ). We used here the notations
$\frac{\partial V}{\partial \vec{r}_{i}} \cdot \vec{r}_{i}=\frac{\partial V}{\partial x_{i}} x_{i}+\frac{\partial V}{\partial y_{i}} y_{i}+\frac{\partial V}{\partial z_{i}} z_{i}$ etc
$\vec{r}_{i} \cdot \frac{\partial^{2} V}{\partial \vec{r}_{i} \partial \vec{r}_{k}} \bullet \vec{r}_{k}=x_{i} \frac{\partial^{2} V}{\partial x_{i} \partial x_{k}} x_{k}+x_{i} \frac{\partial^{2} V}{\partial x_{i} \partial y_{k}} y_{i}+x_{i} \frac{\partial^{2} V}{\partial x_{i} \partial z_{k}} z_{k}+\cdots(6$ more terms ) etc
We shall ignore the first two sums in the curly brackets because they represent quadrupole terms (proportional to $1 / R^{3}$ ) whose contribution to the energy will not vanish only if one of charge distribution is not electrically neutral, in which case there will be more important terms (of order $1 / R^{2}$ ) representing charge-dipole interactions.

The derivatives of $V$ requires the evaluation of the derivatives of $1 / R_{i j}=1 / \sqrt{\left[\left(X-x_{i}+x_{j}^{\prime}\right)^{2}+\left(Y-y_{i}+y_{j}^{\prime}\right)^{2}+\left(Z-z_{i}+z_{j}^{\prime}\right)^{2}\right]}$ at the point $1 / R_{i j}=1 / \mathrm{R}=1 / \sqrt{\left[X^{2}+Y^{2}+Z^{2}\right]}$.

The derivatives are found to be:

$$
\begin{aligned}
& \frac{\partial}{\partial x_{i}} \frac{1}{R_{i j}}=\left.\frac{X-x_{i}-x_{j}^{\prime}}{R_{i j}^{3}}\right|_{x_{x_{i}=x^{\prime}=0}=}=\frac{X}{R^{3}}, \ldots \\
& \frac{\partial}{\partial x_{j}^{\prime}} \frac{1}{R_{i j}}=\left.\frac{X-x_{i}-x_{j}^{\prime}}{R_{i j}^{3}}\right|_{x_{i}=x^{\prime}=0}=-\frac{X}{R^{3}}, \ldots \\
& \frac{\partial^{2}}{\partial x_{i} \partial x_{j}^{\prime}} \frac{1}{R_{i j}}=-\left.\frac{3\left(X-x_{i}-x_{j}^{\prime}\right)^{2}}{R_{i j}^{5}}\right|_{x_{i}=x^{\prime}=0}+\left.\frac{1}{R_{i j}^{3}}\right|_{x_{i}=x_{j}^{\prime}=0}=-\frac{3 X^{2}}{R^{5}}+\frac{1}{R^{3}} \\
& \frac{\partial^{2}}{\partial x_{i} \partial y_{j}^{\prime}} \frac{1}{R_{i j}}=-\left.\frac{3\left(X-x_{i}-x_{j}^{\prime}\right)\left(Y-y_{i}-y_{j}^{\prime}\right)}{R_{i j}^{5}}\right|_{x_{i}=x_{j}^{\prime}=y_{i}=y_{j}^{\prime}=0}=-\frac{3 X Y}{R^{5}}
\end{aligned}
$$

These can be substituted in Eq. (1) to get the desired expression. To simplify this expression we can assume that $\vec{R}$ is parallel to the z axis, which means $X=Y=0$. We then find:

$$
\begin{equation*}
V=\frac{Q Q^{\prime}}{R}+\frac{Q^{\prime} p_{z}-Q p_{z}^{\prime}}{R^{2}}+\frac{p_{x} p_{x}^{\prime}+p_{y} p_{y}^{\prime}-2 p_{z} p_{z}^{\prime}}{R^{3}}+\cdots \tag{4}
\end{equation*}
$$

where

$$
\begin{equation*}
p_{x}=\sum_{i} q_{i} x_{i} \tag{5}
\end{equation*}
$$

is the x component of the dipole moment of the first charge distribution, etc. Eq. (4) is known as the multipole expansion. The first term is the monopole-monopole interaction, the second is monopole-dipole, then comes dipole-dipole and then (not shown) monopole-quadrupole etc.

In the following discussion we shall be mainly interested in the interaction potential between two electrically neutral charge distributions, in which case only the dipole-dipole terms are relevant,

$$
\begin{equation*}
V=\frac{p_{x} p_{x}^{\prime}+p_{y} p_{y}^{\prime}-2 p_{z} p_{z}^{\prime}}{R^{3}}+\cdots(\text { neutral distributions }) \tag{6}
\end{equation*}
$$

It is often convenient to express Eq. (6) in polar coordinated. To this end, let $p=|\vec{p}|=\sqrt{p_{x}^{2}+p_{y}^{2}+p_{z}^{2}}$ denote the magnitude of the dipole moment of the first charge distribution, with an analogous definition of $p^{\prime}$. In polar coordinates, $p_{x}=p \sin \theta \cos \phi, p_{y}=p \sin \theta \sin \phi, p_{z}=p \cos \theta$
and $p_{x}^{\prime}=p^{\prime} \sin \theta^{\prime} \cos \phi^{\prime}, p_{y}^{\prime}=p^{\prime} \sin \theta^{\prime} \sin \phi^{\prime}, p_{z}^{\prime}=p^{\prime} \cos \theta^{\prime}$
It is convenient to use the direction of the $x$ axis of the system to be parallel to the projection of one dipole, say $\vec{p}$, onto the $\mathrm{x}, \mathrm{y}$ plane, so that $\phi \equiv 0$. This means that $p_{x}=p \sin \theta, p_{y}=0, p_{z}=p \cos \theta$ and we obtain

$$
\begin{equation*}
V=V\left(R, \theta, \theta^{\prime}, \phi^{\prime}\right)=\frac{p p^{\prime}}{R^{3}}\left(\sin \theta \sin \theta^{\prime} \cos \phi^{\prime}-2 \cos \theta \cos \theta^{\prime}\right) \tag{7}
\end{equation*}
$$

(remembering that the we have chosen the $z$ to be along $\vec{R}$.)

## Polarizability

In the discussion that follows we shall also need an expression for the polarizability of a charge distribution.

The polarizability of a charge distribution, $\alpha$, is a measure of the dipole moment induced in this distribution by the presence of an external electrical field $\vec{E}$, as defined by the equation:

$$
\begin{equation*}
\vec{p}=\vec{\alpha} \vec{E} \tag{7}
\end{equation*}
$$

The polarizability is actually a tensor, and the notation in the last equation means: $p_{x}=\alpha_{x y} E_{y}$ etc. In other words $\alpha_{x y}$ measures the moment dipole along $x$ induced by an electric field along axis $y$. We shall be mainly interested in symmetrical charge distributions, e.g., atoms or symmetric molecules, in which case $\alpha_{i j}=\alpha \delta_{i j}$ with $\delta_{i j}=1$ if $i=j, \delta_{i j}=0$ if $i \neq j$ denoting the familiar Kronecker Delta function. We shall be mainly concerned with this simpler case, so we can write

$$
\begin{equation*}
\vec{p}=\alpha \vec{E} \tag{8}
\end{equation*}
$$

indicating that the dipole is along the direction of the field.
A schematic illustration depicting the formation of an induced dipole in an electric field is given in Figure 2.

Figure 2


The polarization of the charge distribution upon applying an external electric field involves an energetic price associated with the separation of the charges. To calculate this energy recall that the work done by the field in moving a charge $q$ a small distance $d \vec{r}$ is $d W=q \vec{E} \bullet d \vec{r}$. Suppose now that we gradually increase the magnitude of the electric field (pointing along the z axis) acting on a charge distribution. The incremental work done by the field is given by: $d W=E \sum_{i} q_{i} d z_{i}=E d p=E \alpha d E$ where $d p=d p_{z}$ is the change in the dipole moment of the charge distribution. The total work done by the field in forming the induced dipole is thus given by

$$
\begin{equation*}
W=\int d W=\alpha \int_{0}^{E} E d E=\frac{1}{2} \alpha E^{2} \tag{9}
\end{equation*}
$$

## vdW interactions: Thermal and quantum-mechanical averaging

When considering the interaction energy, $U(R)=\langle V\rangle$, between two molecules possessing permanent dipole moments (e.g., $\mathrm{H}_{2} \mathrm{O}, \mathrm{HCl}$ etc.) we will need to carry out thermal averaging of $V\left(R, \theta, \theta^{\prime}, \phi^{\prime}\right)$ (see Eq. (7) ) over the angles $\theta, \theta^{\prime}, \phi^{\prime}$. This is because certain angles are more probable than others. The averaging involves their Boltzmann weights. Deriving the Boltzmann distribution is an important part of our course and will be discussed in detail separately. Below we shall assume that it is already familiar.

When considering the interaction between two symmetric (non-polar) charge distributions, such as that between atoms or symmetric molecules (e.g., $\mathrm{CH}_{4}$ ) that have no dipole moment, we will have to carry out a quantum-mechanical calculation associated with the interaction between two mutually induced dipole moments, as will be explained in greater detail below. To this end we will need to carry out a quantum-mechanical perturbation theory calculation. A very brief reminder of the basic equations that we will require will be given as needed.

There are three types of long range forces between neutral molecules. The first is between two dipolar molecules and is known as Keesom or dipole-dipole interaction, the second is between a dipolar and a nonpolar molecule. This interaction, first indicated by Debye, is due to the interaction of a permanent dipole with the induced dipole on the neutral molecule. Both Keesom and Debye interactions lead to $1 / \mathrm{R}^{6}$ dependence of the long range interactions. The third type of interaction is between non-polar molecules. Here, momentary fluctuations of the charges (i.e., electrons) on one molecule may result in a momentary dipole moment. This dipole induces a momentary dipole in the second molecule; the two dipoles interact with each other and the interaction continues, following the (partially correlated) transient changes in the two charge distribution. The averaging of these interactions is quantum-mechanical and also leads to a $1 / \mathrm{R}^{6}$ dependence. This last type of interaction was first derived by London and is known as dispersion interaction. All three types of intermolecular forces are collectively called van der Waals forces, because they are responsible for the attractive part of the van der Waals equation. Let us now consider them one by one.

## The interaction between two permanent dipoles (Keesom):

Here we need to average $V\left(R, \theta, \theta^{\prime}, \phi^{\prime}\right)$ over the relative orientations of two dipoles of given magnitudes, $p$ and $p^{\prime}$. The averaging is done using the Boltzmann weights of the different orientational configurations of the two dipoles. That is

$$
\begin{align*}
U_{d d}(R) & =\frac{\int V\left(R, \theta, \theta^{\prime}, \phi^{\prime}\right) e^{-V\left(R, \theta, \theta^{\prime}, \phi^{\prime}\right) / k T} \sin \theta d \theta d \phi \sin \theta^{\prime} d \theta^{\prime} d \phi^{\prime}}{\int e^{-V\left(R, \theta, \theta^{\prime}, \phi^{\prime}\right) / k T} \sin \theta d \theta d \phi \sin \theta^{\prime} d \theta^{\prime} d \phi^{\prime}} \\
& =\frac{\int V[1-V / k T+\cdots] d \Omega d \Omega^{\prime}}{\int[1-V / k T] d \Omega d \Omega^{\prime}}  \tag{10}\\
& =\frac{1}{k T} \frac{p^{2} p^{\prime 2}}{R^{6}} \frac{\int\left(\sin \theta \sin \theta^{\prime} \cos \phi^{\prime}-2 \cos \theta \cos \theta^{\prime}\right)^{2} d \Omega d \Omega^{\prime}}{\int d \Omega d \Omega^{\prime}}
\end{align*}
$$

In the passage from the first to the second equality we have kept the leading terms of the Taylor expansion of the Boltzmann factor, assuming that $V\left(R, \theta, \theta^{\prime}, \phi^{\prime}\right) / k T \ll 1$. Then we note that the linear terms in $V$ in both the numerator and denominators vanish identically following the integration over $d \Omega=\sin \theta d \theta d \phi$ and $d \Omega^{\prime}=\sin \theta^{\prime} d \theta^{\prime} d \phi$ (recall, the range of $\theta, \theta^{\prime}$ is $0 \rightarrow \pi$ and of $\phi, \phi^{\prime}$ is $0 \rightarrow 2 \pi$, so that $\left.\int_{0}^{\pi} \sin \theta d \theta \int_{0}^{2 \pi} d \phi=4 \pi^{2}\right)$. This follows from the fact that :

$$
\begin{aligned}
& \left\langle\cos ^{2} \theta\right\rangle=\frac{1}{4 \pi^{2}} \int_{0}^{\pi} \cos ^{2} \theta \sin \theta d \theta \int_{0}^{2 \pi} d \phi=\frac{1}{3} \\
& \left\langle\sin ^{2} \theta\right\rangle=\frac{2}{3}, \quad\left\langle\sin ^{2} \phi\right\rangle=\left\langle\cos ^{2} \phi\right\rangle=\frac{1}{2} \\
& \langle\sin \theta\rangle=\langle\cos \theta\rangle=\langle\sin \theta \cos \theta\rangle=0 \\
& \langle\sin \phi\rangle=\langle\cos \phi\rangle=\langle\sin \phi \cos \phi\rangle=0
\end{aligned}
$$

With similar results for the "primed" charge distribution. Given all these integrals we find:

$$
\begin{equation*}
U(R)=\frac{2}{3 k T} \frac{p^{2} p^{\prime 2}}{R^{6}} \tag{Keesom}
\end{equation*}
$$

## The interaction between a permanent dipole and an induced dipole (Debye):

In this case, a dipolar charge distribution interacts with a non-polar one. The permanent dipole of the polar charge distribution, e.g., an HCl molecule, induces a dipole in another molecule, and the permanent and induced dipoles interact with each other. To calculate the interaction energy suppose that the permanent dipole is of magnitude $p$ and is directed along the z axis. It can be shown that the magnitude of the electric field at an arbitrary point at distance $R$ (far from the dipole) and angle $\theta$ with respect to the z axis (the dipole direction) is given by:

$$
\begin{equation*}
E=\frac{p}{R^{3}}\left(3 \cos ^{2} \theta+1\right)^{1 / 2} \tag{12}
\end{equation*}
$$

Using $R$ and $\theta$ to denote the position of the neutral charge distribution relative to the dipole, its polarization to form an induced dipole can be described as a gradual process involving the gradual charging of the permanent dipole, as accounted for by Eq (9). From Eqs (9) and (12) we thus obtain the Debye interaction energy:

$$
U(R, \theta)=\frac{1}{2} \frac{\alpha p^{2}}{R^{6}}\left(3 \cos ^{2} \theta+1\right)
$$

Further averaging over $\theta$ (and recall $\left\langle\cos ^{2} \theta\right\rangle=1 / 3$ we find

$$
\begin{equation*}
U(R, \theta)=\frac{\alpha p^{2}}{R^{6}} \quad \text { Debye } \tag{13}
\end{equation*}
$$

Note also that permanent dipoles induce dipoles in polar molecules as well. The interaction between the permanent and induced dipoles adds to the interaction between the two permanent dipoles.

## Dispersion interaction between two non-polar molecules (London):

The interaction energy between two electrically neutral non-polar molecules, A and B, involves the dipolar interactions between transient momentary dipoles on one molecule and induced dipoles on the other. This interaction is purely quantum-mechanical and will be calculated using perturbation theory, with the dipole-dipole interaction potential (see Eq. (6))

$$
\begin{equation*}
V=\frac{p_{x}^{A} p_{x}^{B}+p_{y}^{A} p_{y}^{B}-2 p_{z}^{A} p_{z}^{B}}{R^{3}} \tag{14}
\end{equation*}
$$

representing the quantum-mechanical perturbation operator. That is, the Hamiltonian of the system is given by:

$$
\begin{equation*}
H=H_{0}+V=H_{A}+H_{B}+V \tag{15}
\end{equation*}
$$

with $H_{0}=H_{A}+H_{B}$, the unperturbed Hamiltonian is the sum of the independent (noninteracting) molecules A and B .

Using the Dirac notation, let $|\lambda\rangle=\left|n_{A}^{0}, n_{B}^{0}\right\rangle$ denote the unperturbed wave functions, i.e.,

$$
\begin{equation*}
H_{0}|\lambda\rangle=\left(H_{A}+H_{B}\right)\left|n_{A}^{0}, n_{B}^{0}\right\rangle=\left(E_{n_{A}}^{0}+E_{n_{B}}^{0}\right)\left|n_{A}^{0}, n_{B}^{0}\right\rangle=E_{\lambda}^{0}|\lambda\rangle \tag{16}
\end{equation*}
$$

with $\left|n_{A}^{0}\right\rangle$ and $\left|n_{B}^{0}\right\rangle$ representing the unperturbed wave functions of $A$ and $B$, respectively.
According to perturbation theory, the interaction energy between $A$ and $B$ is given by

$$
\begin{align*}
\Delta E & =\Delta E^{(1)}+\Delta E^{(2)}+\cdots \\
& =\langle\lambda=0| V|\lambda=0\rangle-\sum_{\lambda>0} \frac{\langle 0| V|\lambda\rangle\langle\lambda| V|0\rangle}{E_{\lambda}-E_{0}}+\cdots  \tag{17}\\
& =\langle 0,0| V|0,0\rangle-\sum_{n_{A}^{0}>0, n_{B}^{0}>0} \frac{\langle 0,0| V\left|n_{A}^{0}, n_{B}^{0}\right\rangle\left\langle n_{A}^{0}, n_{B}^{0}\right| V|0,0\rangle}{E_{n_{A}}^{0}+E_{n_{B}}^{0}-E_{0_{A}}^{0}+E_{0_{B}}^{0}}+\cdots
\end{align*}
$$

with $\langle 0,0| V|0,0\rangle=\left\langle n_{A}^{0}=0, n_{B}^{0}=0\right| V\left|n_{A}^{0}=0, n_{B}^{0}=0\right\rangle$ etc.
Now we have to substitute $V$ from Eq. (15) and evaluate the matrix elements. Since nonpolar do not have a dipole moment, certainly not in the ground state, the first order correction vanishes identically. Explicitly, this follows from the fact that:

$$
\begin{equation*}
\langle 0,0| p_{x}^{A} p_{x}^{B}|0,0\rangle=\langle 0| p_{x}^{A}|0\rangle\langle 0| p_{x}^{B}|0\rangle \equiv 0 \tag{18}
\end{equation*}
$$

We are thus left with the second order term, and we see immediately that it is also proportional to $1 / R^{6}$. Namely,

$$
\begin{align*}
U_{d i s}(R) & =\Delta E^{(2)}=-\sum_{n_{A}^{0}>0, n_{B}^{0}>0} \frac{\langle 0,0| V\left|n_{A}^{0}, n_{B}^{0}\right\rangle\left\langle n_{A}^{0}, n_{B}^{0}\right| V|0,0\rangle}{E_{n_{A}}^{0}+E_{n_{B}}^{0}-E_{0_{A}}^{0}+E_{0_{B}}^{0}} \\
& \approx-\frac{1}{\left(I_{A}+I_{B}\right)} \sum_{n_{A}^{0}>0, n_{B}^{0}>0}\langle 0,0| V\left|n_{A}^{0}, n_{B}^{0}\right\rangle\left\langle n_{A}^{0}, n_{B}^{0}\right| V|0,0\rangle  \tag{19}\\
& =-\frac{1}{\left(I_{A}+I_{B}\right)} \sum_{n_{A}^{0}, n_{B}^{0}}\left[\langle 0,0| V\left|n_{A}^{0}, n_{B}^{0}\right\rangle\left\langle n_{A}^{0}, n_{B}^{0}\right| V|0,0\rangle\right]-\langle 0,0| V|0,0\rangle\langle 0,0| V|0,0\rangle \\
& =-\frac{1}{\left(I_{A}+I_{B}\right)}\langle 0,0| V^{2}|0,0\rangle
\end{align*}
$$

The passage from the first to the second line in Eq. (19) is based on the approximation whereby all the excitation energies are replaced by the ionization potential, i.e., $E_{n_{A}}^{0}-E_{0_{A}}^{0} \rightarrow I_{A}$ etc. This is a common and generally very good approximation, providing a lower bound to the magnitude of the interaction. In passing from the second to the third line we extended the sum to all $n_{A}^{0}, n_{B}^{0}$ and subtracted the first term, $\langle 0,0| V|0,0\rangle\langle 0,0| V|0,0\rangle$, which as noted above (see Eq. (18)) is identically zero. Finally, in passing to the last line we have used the general mathematical identity

$$
\begin{equation*}
\sum_{m}\langle 0| A|m\rangle\langle m| A|0\rangle=\langle 0| A^{2}|0\rangle \tag{20}
\end{equation*}
$$

where $A$ is any Hermitian operator.
Now, combining Eqs. (14) and (19) we find

$$
\left.\begin{array}{rl}
U_{d i s}(R)= & \Delta E^{(2)}=-\frac{1}{R^{6}} \frac{1}{\left(I_{A}+I_{B}\right)}\langle 0,0|\left(p_{x}^{A} p_{x}^{B}+p_{y}^{A} p_{y}^{B}-2 p_{z}^{A} p_{z}^{B}\right)^{2}|0,0\rangle \\
= & -\frac{1}{R^{6}} \frac{1}{\left(I_{A}+I_{B}\right)}\left[\langle 0|\left(p_{x}^{A}\right)^{2}|0\rangle\langle 0|\left(p_{x}^{B}\right)^{2}|0\rangle\right. \tag{21}
\end{array}+\langle 0|\left(p_{y}^{A}\right)^{2}|0\rangle\langle 0|\left(p_{y}^{B}\right)^{2}|0\rangle\right\}
$$

In passing to the second equality we noticed that all terms that are linear in $p_{x}^{A}$, $p_{x}^{B}$, etc., such as $p_{x}^{A} p_{x}^{B} p_{y}^{A} p_{y}^{B}$ etc. vanish identically. The third line is valid for symmetric molecules, in which case all six terms in the square brackets make identical contribution. Finally, if A and B have symmetric charge distribution, as is the case for atoms and symmetrical molecules, then we find

$$
\begin{equation*}
U_{d i s}(R)=-\frac{6}{R^{6}} \frac{1}{\left(I_{A}+I_{B}\right)}\langle 0|\left(p_{x}^{A}\right)^{2}|0\rangle\langle 0|\left(p_{x}^{B}\right)^{2}|0\rangle \tag{22}
\end{equation*}
$$

## Relating $U_{\text {dis }}(R)$ to the polarizabilities of the interacting molecules: London's formula

The polarizability of a molecule can also be calculated by perturbation theory. The starting point for such a calculation is the Hamiltonian of a molecule in an electric field. Assuming that the field is along the z axis,

$$
H=H_{0}+V=H_{0}+E_{z} \sum_{i} q_{i} z_{i}=H_{0}+E_{z} p_{z}
$$

Let $|n\rangle$ denote the n'th quantum state of the full (i.e., the perturbed) Hamiltonian, H. From perturbation theory:

$$
|n\rangle=\left|n^{(0)}\right\rangle+\left|n^{(1)}\right\rangle+\left|n^{(2)}\right\rangle+\cdots
$$

with $\left|n^{(0)}\right\rangle$ denoting the eigenstates of $H_{0}$. The first order correction to the wave function is given by

$$
\left|n^{(1)}\right\rangle=-\sum_{m \neq n} \frac{\left\langle m^{(0)}\right| V\left|n^{(0)}\right\rangle}{E_{m}^{(0)}-E_{n}^{(0)}}\left|m^{(0)}\right\rangle \equiv-\sum_{m \neq n} \frac{V_{m n}}{E_{m}^{(0)}-E_{n}^{(0)}}\left|m^{(0)}\right\rangle
$$

with

$$
\begin{aligned}
\left\langle m^{(0)}\right| V\left|n^{(0)}\right\rangle & =V_{m n}=E_{z}\left\langle m^{(0)}\right| p_{z}\left|n^{(0)}\right\rangle=E_{z}\left(p_{z}\right)_{m n} \\
& =E_{z} \sum_{i} q_{i}\left(z_{i}\right)_{m n}
\end{aligned}
$$

The expectation value of the dipole moment in the perturbed system is given by

$$
\begin{aligned}
\langle n| p_{z}|n\rangle & =\left\langle n^{(0)}\right| p_{z}\left|n^{(0)}\right\rangle+\left\langle n^{(0)}\right| p_{z}\left|n^{(1)}\right\rangle+\left\langle n^{(1)}\right| p_{z}\left|n^{(0)}\right\rangle+\cdots \\
& =\left\langle n^{(0)}\right| p_{z}\left|n^{(0)}\right\rangle+2\left\langle n^{(0)}\right| p_{z}\left|n^{(1)}\right\rangle \\
& =\left(p_{z}\right)_{n n}^{(0)}+\left(p_{z}\right)_{n n}^{(1)}+\cdots
\end{aligned}
$$

The zero order term is zero for non-polar molecules, thus $\left\langle n^{(0)}\right| p_{z}\left|n^{(0)}\right\rangle=0$. For the first order term we find:

$$
\begin{aligned}
\langle n| p_{z}|n\rangle & \left.\approx\left(p_{z}\right)_{n n}^{(1)}=2\left\langle n^{(0)}\right| p_{z}\left|n^{(1)}\right\rangle=2\left\langle n^{(0)}\right| p_{z}\left|\sum_{m \neq n} \frac{V_{m n}}{E_{m}^{(0)}-E_{n}^{(0)}}\right| m^{(0)}\right\rangle \\
& =2 E_{z} \sum_{m \neq n} \frac{\left\langle n^{(0)}\right| p_{z}\left|m^{(0)}\right\rangle\left\langle m^{(0)}\right| p_{z}\left|n^{(0)}\right\rangle}{E_{m}^{(0)}-E_{n}^{(0)}}
\end{aligned}
$$

We are mainly interested in the ground state, $n=0$. Using the approximation used earlier, namely $E_{m}^{(0)}-E_{0}^{(0)} \approx I$, we find

$$
\begin{aligned}
\langle 0| p_{z}|0\rangle & \approx \frac{2 E_{z}}{I} \sum_{m \neq 0}\langle 0| p_{z}\left|m^{(0)}\right\rangle\left\langle m^{(0)}\right| p_{z}|0\rangle \\
& \left.=\frac{2 E_{z}}{I} \sum_{m=0}\langle 0| p_{z}\left|m^{(0)}\right\rangle\left\langle m^{(0)}\right| p_{z}|0\rangle-\left|\langle 0| p_{z}\right| 0\right\rangle\left.\right|^{2} \\
& \left.=\frac{2 E_{z}}{I}\left|\langle 0| p_{z}{ }^{2}\right| 0\right\rangle\left.\right|^{2}
\end{aligned}
$$

This means that the polarizability is given by

$$
\left.\alpha=\frac{2}{I}\left|\langle 0| p_{z}{ }^{2}\right| 0\right\rangle\left.\right|^{2}
$$

Comparing this result with the expression derived earlier for the dispersion interaction (Eq. (22)) we find (noting that there is no difference between the $\mathrm{x}, \mathrm{y}$ and z directions):

$$
U_{d i s}(R)=-\frac{1}{R^{6}} \frac{3 I_{A} I_{B}}{\left(I_{A}+I_{B}\right)} \alpha_{A} \alpha_{B}
$$

This famous expression is known as London's formula.

