Intermolecular force fields
and how they can be determined

Ad van der Avoird

University of Nijmegen

Equation of state (Van der Waals) of *non-ideal* gas

$$\left(p + \frac{a}{V^2}\right)\left(V - b\right) = kT$$

repulsion $\Rightarrow$ b (eigenvolume)

attraction $\Rightarrow$ a (reduced pressure)

Virial expansion (density $\rho = 1/V$)

$$p = kT\left[\rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \ldots\right]$$

with

$$B_2(T) = -\frac{1}{2}\int_0^\infty \left[\exp\left(-\frac{\Delta E(R)}{kT}\right) - 1\right] 4\pi R^2\, dR$$

Intermolecular forces

Intermolecular forces

1909 / 1912

Reinganum, Debye: dipole-dipole, attractive when orientations are averaged over thermal motion

Intermolecular forces

1909 / 1912

Reinganum, Debye: dipole-dipole, attractive when orientations are averaged over thermal motion

1920 / 1921

Debye, Keesom: dipole (quadrupole) - induced dipole (attractive)

Intermolecular forces

1909 / 1912

Reinganum, Debye: dipole-dipole, attractive when orientations are averaged over thermal motion

1920 / 1921

Debye, Keesom: dipole (quadrupole) - induced dipole (attractive)

1927

Heitler & London: Quantum mechanics (QM)

$\Rightarrow$ covalent bonding for singlet H_2 ($S = 0$)

$\Rightarrow$ exchange repulsion for triplet H_2 ($S = 1$)

Intermolecular forces

1909 / 1912

Reinganum, Debye: dipole-dipole, attractive when orientations are averaged over thermal motion

1920 / 1921

Debye, Keesom: dipole (quadrupole) - induced dipole (attractive)

1927

Heitler & London: Quantum mechanics (QM)

$\Rightarrow$ covalent bonding for singlet H_2 ($S = 0$)

$\Rightarrow$ exchange repulsion for triplet H_2 ($S = 1$)

1927 / 1930

Wang, London: QM $\Rightarrow$ dispersion forces (attractive)

QM derivation of intermolecular forces

correspondence with classical electrostatics

QM derivation of intermolecular forces

correspondence with classical electrostatics

Intermezzo:

(Time-independent) perturbation theory

Schrödinger equation $H\Phi = E\Phi$ not exactly solvable.

Perturbation theory $\Rightarrow$ Approximate solutions E_k and Φ_k

Schrödinger equation $H\Phi = E\Phi$ not exactly solvable.

Perturbation theory $\Rightarrow$ Approximate solutions E_k and Φ_k

Find simpler Hamiltonian $H^{(0)}$ for which $H^{(0)}\Phi^{(0)} = E^{(0)}\Phi^{(0)}$ is solvable, with solutions $E_k^{(0)}$ and $\Phi_k^{(0)}$

“Perturbation” $H^{(1)} = H - H^{(0)}$

Write $H(\lambda) = H^{(0)} + \lambda H^{(1)}$ (switch parameter λ)

$$\begin{array}{ccc}
0 & \xrightarrow{\lambda} & 1 \\
H^{(0)} & \xrightarrow{H(\lambda)} & H \\
E_k^{(0)} & \xrightarrow{E_k(\lambda)} & E_k \\
\Phi_k^{(0)} & \xrightarrow{\Phi_k(\lambda)} & \Phi_k
\end{array}$$

Expand

$$\begin{aligned} E_k(\lambda) &= E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \ldots \\ \Phi_k(\lambda) &= \Phi_k^{(0)} + \lambda \Phi_k^{(1)} + \lambda^2 \Phi_k^{(2)} + \ldots \end{aligned}$$

Expand

$$\begin{aligned} E_k(\lambda) &= E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \ldots \\ \Phi_k(\lambda) &= \Phi_k^{(0)} + \lambda \Phi_k^{(1)} + \lambda^2 \Phi_k^{(2)} + \ldots \end{aligned}$$

Substitution into $H(\lambda)\Phi_k(\lambda) = E_k(\lambda)\Phi_k(\lambda)$ and equating each power of λ yields, after some manipulations

$$E_k^{(1)} = \langle\ \Phi_k^{(0)} \mid H^{(1)} \mid \Phi_k^{(0)}\ \rangle$$

$$E_k^{(2)} = \sum_{i \neq k} \frac{\langle\ \Phi_k^{(0)} \mid H^{(1)} \mid \Phi_i^{(0)}\ \rangle\langle\ \Phi_i^{(0)} \mid H^{(1)} \mid \Phi_k^{(0)}\ \rangle}{E_k^{(0)} - E_i^{(0)}}$$

Used to calculate perturbation corrections of $E_k^{(0)}$

First perturbation correction of $\Phi_k^{(0)}$

$$\Phi_k^{(1)} = \sum_{i \neq k} \frac{\langle \; \Phi_i^{(0)} \mid H^{(1)} \mid \Phi_k^{(0)} \; \rangle}{E_k^{(0)} - E_i^{(0)}} \Phi_i^{(0)}$$

First perturbation correction of $\Phi_k^{(0)}$

$$\Phi_k^{(1)} = \sum_{i \neq k} \frac{\langle\ \Phi_i^{(0)} \mid H^{(1)} \mid \Phi_k^{(0)}\ \rangle}{E_k^{(0)} - E_i^{(0)}} \Phi_i^{(0)}$$

The second order energy may also be written as

$$E_k^{(2)} = \langle\ \Phi_k^{(0)} \mid H^{(1)} \mid \Phi_k^{(1)}\ \rangle$$

Molecule in electric field

External potential $V(\boldsymbol{r}) = V(x, y, z)$

Molecule in electric field

External potential $V(\boldsymbol{r}) = V(x, y, z)$

Particles i with charge q_i (nuclei $q_i = Z_i e$, electrons $q_i = -e$)

Molecule in electric field

External potential $V(\boldsymbol{r}) = V(x, y, z)$

Particles i with charge q_i (nuclei $q_i = Z_i e$, electrons $q_i = -e$)

Hamiltonian $H = H^{(0)} + H^{(1)}$

with free molecule Hamiltonian $H^{(0)}$

and perturbation

$$H^{(1)} = \sum_{i=1}^{n} q_i V(\boldsymbol{r}_i) = \sum_{i=1}^{n} q_i V(x_i, y_i, z_i)$$

Multipole (Taylor) expansion

$$V(x,y,z) = V_0 + x\left(\frac{\partial V}{\partial x}\right)_0 + y\left(\frac{\partial V}{\partial y}\right)_0 + z\left(\frac{\partial V}{\partial z}\right)_0 + \ldots$$

with electric field $\boldsymbol{F} = (F_x, F_y, F_z) = -\mathrm{grad}\ V$

$$V(\boldsymbol{r}) = V(x,y,z) = V_0 - \boldsymbol{r}\cdot\boldsymbol{F}_0 + \ldots$$

Multipole (Taylor) expansion

$$V(x,y,z) = V_0 + x\left(\frac{\partial V}{\partial x}\right)_0 + y\left(\frac{\partial V}{\partial y}\right)_0 + z\left(\frac{\partial V}{\partial z}\right)_0 + \dots$$

with electric field $\boldsymbol{F} = (F_x, F_y, F_z) = -\mathrm{grad}\ V$

$$V(\boldsymbol{r}) = V(x,y,z) = V_0 - \boldsymbol{r}\cdot\boldsymbol{F}_0 + \dots$$

Perturbation operator

$$H^{(1)} = qV_0 - \boldsymbol{\mu}\cdot\boldsymbol{F}_0 + \dots$$

with total charge $q = \sum_{i=1}^{n} q_i$ and dipole operator $\boldsymbol{\mu} = \sum_{i=1}^{n} q_i\boldsymbol{r}_i$

First order perturbation energy (for ground state $k = 0$)

$$\begin{aligned} E_0^{(1)} &= \langle\, \Phi_0^{(0)} \mid H^{(1)} \mid \Phi_0^{(0)} \,\rangle \\ &= \langle\, \Phi_0^{(0)} \mid -\boldsymbol{\mu} \cdot \boldsymbol{F}_0 + \ldots \mid \Phi_0^{(0)} \,\rangle \\ &= -\langle\, \Phi_0^{(0)} \mid \boldsymbol{\mu} \mid \Phi_0^{(0)} \,\rangle \cdot \boldsymbol{F}_0 + \ldots \\ &= -\langle\, \boldsymbol{\mu} \,\rangle \cdot \boldsymbol{F}_0 + \ldots \end{aligned}$$

First order perturbation energy (for ground state $k = 0$)

$$\begin{aligned} E_0^{(1)} &= \langle\, \Phi_0^{(0)} \mid H^{(1)} \mid \Phi_0^{(0)} \,\rangle \\ &= \langle\, \Phi_0^{(0)} \mid -\boldsymbol{\mu} \cdot \boldsymbol{F}_0 + \ldots \mid \Phi_0^{(0)} \,\rangle \\ &= -\langle\, \Phi_0^{(0)} \mid \boldsymbol{\mu} \mid \Phi_0^{(0)} \,\rangle \cdot \boldsymbol{F}_0 + \ldots \\ &= -\langle\, \boldsymbol{\mu} \,\rangle \cdot \boldsymbol{F}_0 + \ldots \end{aligned}$$

Energy of permanent dipole $\langle\, \boldsymbol{\mu} \,\rangle$ in field $\boldsymbol{F}_0$.
Same as classical electrostatics, with dipole $\langle\, \boldsymbol{\mu} \,\rangle$.

Second order perturbation energy

for neutral molecule ($q = 0$) and field in z-direction

i.e., $\boldsymbol{F}_0 = (0, 0, F_0)$ and $H^{(1)} = -\mu_z F_0$

$$\begin{aligned} E_0^{(2)} &= \sum_{i \neq 0} \frac{\langle\ \Phi_0^{(0)} \mid H^{(1)} \mid \Phi_i^{(0)}\ \rangle \langle\ \Phi_i^{(0)} \mid H^{(1)} \mid \Phi_0^{(0)}\ \rangle}{E_0^{(0)} - E_i^{(0)}} \\ &= \left[\sum_{i \neq 0} \frac{\langle\ \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)}\ \rangle \langle\ \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)}\ \rangle}{E_0^{(0)} - E_i^{(0)}} \right] F_0^2 \end{aligned}$$

Second order perturbation energy

for neutral molecule ($q = 0$) and field in z-direction

i.e., $\boldsymbol{F}_0 = (0, 0, F_0)$ and $H^{(1)} = -\mu_z F_0$

$$\begin{aligned} E_0^{(2)} &= \sum_{i\neq 0} \frac{\langle\, \Phi_0^{(0)} \mid H^{(1)} \mid \Phi_i^{(0)} \,\rangle\langle\, \Phi_i^{(0)} \mid H^{(1)} \mid \Phi_0^{(0)} \,\rangle}{E_0^{(0)} - E_i^{(0)}} \\ &= \left[\sum_{i\neq 0} \frac{\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)} \,\rangle\langle\, \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle}{E_0^{(0)} - E_i^{(0)}}\right] F_0^2 \end{aligned}$$

Same as classical electrostatics: $E_{\mathrm{pol}} = -\frac{1}{2}\alpha F_0^2$,
with polarizability

$$\alpha_{zz} = 2 \sum_{i \neq 0} \frac{\langle\ \Phi_0^{(0)}\ |\ \mu_z\ |\ \Phi_i^{(0)}\ \rangle \langle\ \Phi_i^{(0)}\ |\ \mu_z\ |\ \Phi_0^{(0)}\ \rangle}{E_i^{(0)} - E_0^{(0)}}$$

$$\alpha_{zz} = 2 \sum_{i \neq 0} \frac{\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)} \,\rangle \langle\, \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle}{E_i^{(0)} - E_0^{(0)}}$$

The polarizability α_{zz} can also be obtained from the induced dipole moment. The total dipole moment is

$$\langle\, \Phi_0^{(0)} + \Phi_0^{(1)} \mid \mu_z \mid \Phi_0^{(0)} + \Phi_0^{(1)} \,\rangle =$$

$$\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle + 2\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle + \langle\, \Phi_0^{(1)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle$$

$$\alpha_{zz} = 2 \sum_{i \neq 0} \frac{\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)} \,\rangle \langle\, \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle}{E_i^{(0)} - E_0^{(0)}}$$

The polarizability α_{zz} can also be obtained from the induced dipole moment. The total dipole moment is

$$\langle\, \Phi_0^{(0)} + \Phi_0^{(1)} \mid \mu_z \mid \Phi_0^{(0)} + \Phi_0^{(1)} \,\rangle =$$

$$\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle + 2 \langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle + \langle\, \Phi_0^{(1)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle$$

The (first order) induced dipole moment μ_{ind} is the second term. With the first order wave function

$$\Phi_0^{(1)} = \sum_{i \neq 0} \frac{\langle\, \Phi_i^{(0)} \mid H^{(1)} \mid \Phi_0^{(0)} \,\rangle}{E_0^{(0)} - E_i^{(0)}} \Phi_i^{(0)}$$

and $H^{(1)} = -\mu_z F_0$ this yields

$$\begin{aligned} \mu_{\rm ind} &= 2\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle \\ &= \left[2 \sum_{i\neq 0} \frac{\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)} \,\rangle\langle\, \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle}{E_i^{(0)} - E_0^{(0)}} \right] F_0 \end{aligned}$$

and $H^{(1)} = -\mu_z F_0$ this yields

$$\begin{aligned}\mu_{\mathrm{ind}} &= 2\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle \\ &= \left[2 \sum_{i \neq 0} \frac{\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)} \,\rangle \langle\, \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle}{E_i^{(0)} - E_0^{(0)}} \right] F_0\end{aligned}$$

As in classical electrostatics: $\mu_{\mathrm{ind}} = \alpha F_0$, with the same formula for the polarizability α_{zz} as above.

and $H^{(1)} = -\mu_z F_0$ this yields

$$\begin{aligned} \mu_{\text{ind}} &= 2\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle \\ &= \left[2 \sum_{i \neq 0} \frac{\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)} \,\rangle\langle\, \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle}{E_i^{(0)} - E_0^{(0)}} \right] F_0 \end{aligned}$$

As in classical electrostatics: $\mu_{\text{ind}} = \alpha F_0$, with the same formula for the polarizability α_{zz} as above.

For arbitrary molecules the direction of the induced dipole moment $\boldsymbol{\mu}_{\text{ind}}$ is not parallel to $\boldsymbol{F}_0$. The polarizability $\boldsymbol{\alpha}$ is a second rank tensor with non-zero elements α_{xy}, etc.

and $H^{(1)} = -\mu_z F_0$ this yields

$$\begin{aligned} \mu_{\text{ind}} &= 2\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_0^{(1)} \,\rangle \\ &= \left[2\sum_{i\neq 0} \frac{\langle\, \Phi_0^{(0)} \mid \mu_z \mid \Phi_i^{(0)} \,\rangle\langle\, \Phi_i^{(0)} \mid \mu_z \mid \Phi_0^{(0)} \,\rangle}{E_i^{(0)} - E_0^{(0)}} \right] F_0 \end{aligned}$$

As in classical electrostatics: $\mu_{\text{ind}} = \alpha F_0$, with the same formula for the polarizability α_{zz} as above.

For arbitrary molecules the direction of the induced dipole moment $\boldsymbol{\mu}_{\text{ind}}$ is not parallel to $\boldsymbol{F}_0$. The polarizability $\boldsymbol{\alpha}$ is a second rank tensor with non-zero elements α_{xy}, etc.

For isotropic systems (atoms, freely rotating molecules) $\boldsymbol{\alpha}$ is diagonal and $\alpha_{xx} = \alpha_{yy} = \alpha_{zz} = \alpha$.

Long range interactions between two molecules

Molecules A and B at distance R with no overlap of their wave functions. Particles $i \in A$ and $j \in B$.

Long range interactions between two molecules

Molecules A and B at distance R with no overlap of their wave functions. Particles $i \in A$ and $j \in B$.

Hamiltonian $H = H^{(0)} + H^{(1)}$ with free molecule Hamiltonian $H^{(0)} = H^A + H^B$ and interaction operator

$$H^{(1)} = \sum_{i \in A} \sum_{j \in B} \frac{q_i q_j}{r_{ij}}$$

Long range interactions between two molecules

Molecules A and B at distance R with no overlap of their wave functions. Particles $i \in A$ and $j \in B$.

Hamiltonian $H = H^{(0)} + H^{(1)}$ with free molecule Hamiltonian $H^{(0)} = H^A + H^B$ and interaction operator

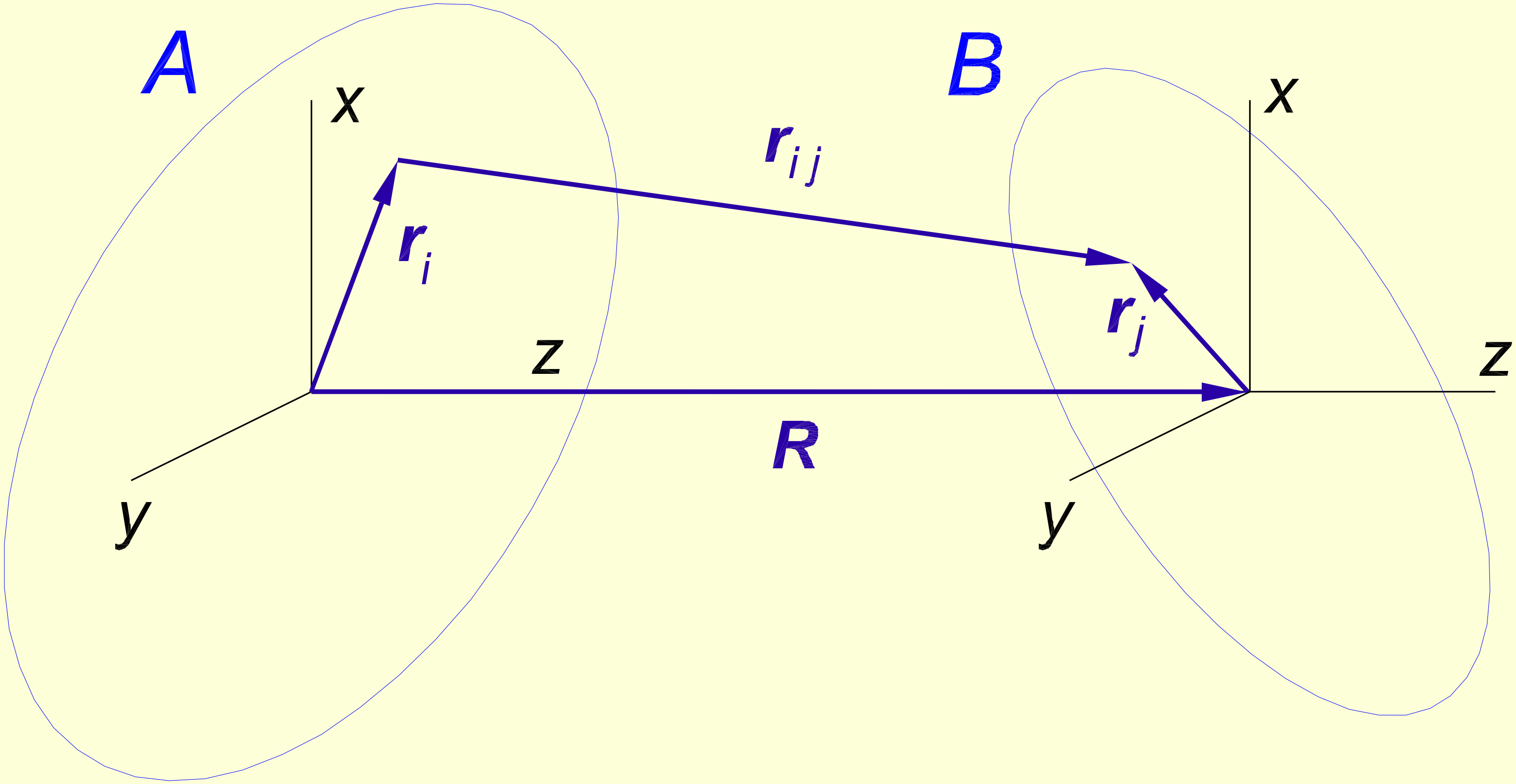
$$H^{(1)} = \sum_{i \in A} \sum_{j \in B} \frac{q_i q_j}{r_{ij}}$$

Same as $H^{(1)} = \sum_{i=1}^{n} q_i V(\boldsymbol{r}_i)$ in previous section with

molecule A in electric potential $V(\boldsymbol{r}_i) = \sum_{j \in B} \frac{q_j}{r_{ij}}$

of molecule B.

Multipole expansion of the interaction operator



$$\boldsymbol{r}_i = (x_i, y_i, z_i), \quad \boldsymbol{r}_j = (x_j, y_j, z_j), \quad \boldsymbol{R} = (0, 0, R)$$

$$\boldsymbol{r}_{ij} = \boldsymbol{r}_j - \boldsymbol{r}_i + \boldsymbol{R} \quad \text{and} \quad r_{ij} = |\boldsymbol{r}_{ij}|$$

A double Taylor expansion in (x_i, y_i, z_i) and (x_j, y_j, z_j) of

$$\frac{1}{r_{ij}} = \left[(x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i + R)^2\right]^{-1/2}$$

at $(x_i, y_i, z_i) = (0,0,0)$ and $(x_j, y_j, z_j) = (0,0,0)$ yields

$$\frac{1}{r_{ij}} = \frac{1}{R} + \frac{z_i}{R^2} - \frac{z_j}{R^2} + \frac{x_i x_j + y_i y_j - 2 z_i z_j}{R^3} + \dots$$

This expansion converges when $|\boldsymbol{r}_i| + |\boldsymbol{r}_j| < R$.

Substitution into $H^{(1)}$ gives, after some rearrangement

$$H^{(1)} = \frac{q^A q^B}{R} + \frac{\mu_z^A q^B}{R^2} - \frac{q^A \mu_z^B}{R^2} + \frac{\mu_x^A \mu_x^B + \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B}{R^3}$$

with the total charges $q^A = \sum_{i \in A} q_i \quad q^B = \sum_{j \in B} q_j$

and the dipole operators $\boldsymbol{\mu}^A = \sum_{i \in A} q_i \boldsymbol{r}_i \quad \boldsymbol{\mu}^B = \sum_{j \in B} q_j \boldsymbol{r}_j$

Substitution into $H^{(1)}$ gives, after some rearrangement

$$H^{(1)} = \frac{q^A q^B}{R} + \frac{\mu_z^A q^B}{R^2} - \frac{q^A \mu_z^B}{R^2} + \frac{\mu_x^A \mu_x^B + \mu_y^A \mu_y^B - 2\mu_z^A \mu_z^B}{R^3}$$

with the total charges $q^A = \sum_{i \in A} q_i \quad q^B = \sum_{j \in B} q_j$

and the dipole operators $\boldsymbol{\mu}^A = \sum_{i \in A} q_i \boldsymbol{r}_i \quad \boldsymbol{\mu}^B = \sum_{j \in B} q_j \boldsymbol{r}_j$

This operator $H^{(1)}$ includes the electrostatic interactions between the charges and dipole moments of the molecules A and B. Higher (quadrupole) interactions are neglected.

Alternative forms of the dipole-dipole interaction operator are

$$\frac{\mu_x^A\mu_x^B + \mu_y^A\mu_y^B - 2\mu_z^A\mu_z^B}{R^3} = \frac{\boldsymbol{\mu}^A \cdot \boldsymbol{\mu}^B - 3\mu_z^A\mu_z^B}{R^3} = \frac{\boldsymbol{\mu}^A \cdot \boldsymbol{T} \cdot \boldsymbol{\mu}^B}{R^3}$$

with the interaction tensor

$$\boldsymbol{T} = \begin{pmatrix} T_{xx} & T_{xy} & T_{xz} \\ T_{yz} & T_{yy} & T_{yz} \\ T_{zx} & T_{zy} & T_{zz} \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{pmatrix}$$

This tensor can also be expressed in more general coordinates.

The solutions of the Schrödinger equations of the free molecules A and B are

$$\begin{aligned} H^A \Phi^A_{k_1} &= E^A_{k_1} \Phi^A_{k_1} \\ H^B \Phi^A_{k_2} &= E^B_{k_2} \Phi^B_{k_2} \end{aligned}$$

and of the unperturbed problem

$$H^{(0)} \Phi^{(0)}_K = E^{(0)}_K \Phi^{(0)}_K$$

with $\Phi^{(0)}_K = \Phi^A_{k_1} \Phi^B_{k_2}$ and eigenvalues $E^{(0)}_K = E^A_{k_1} + E^B_{k_2}$

Proof

$$\begin{aligned}
H^{(0)}\Phi_K^{(0)} &= \left(H^A + H^B\right)\Phi_{k_1}^A\Phi_{k_2}^A \\
&= \left(H^A\Phi_{k_1}^A\right)\Phi_{k_2}^B + \Phi_{k_1}^A\left(H^B\Phi_{k_2}^B\right) \\
&= \left(E_{k_1}^A + E_{k_2}^B\right)\Phi_{k_1}^A\Phi_{k_2}^B
\end{aligned}$$

Proof

$$
\begin{aligned}
H^{(0)}\Phi_K^{(0)} &= \left(H^A + H^B\right)\Phi_{k_1}^A\,\Phi_{k_2}^A \\
&= \left(H^A\Phi_{k_1}^A\right)\Phi_{k_2}^B + \Phi_{k_1}^A\left(H^B\Phi_{k_2}^B\right) \\
&= \left(E_{k_1}^A + E_{k_2}^B\right)\Phi_{k_1}^A\,\Phi_{k_2}^B
\end{aligned}
$$

Perturbation operator (repeated)

$$
H^{(1)} = \frac{q^A q^B}{R} + \frac{\mu_z^A q^B}{R^2} - \frac{q^A \mu_z^B}{R^2} + \frac{\boldsymbol{\mu}^A \cdot \boldsymbol{T} \cdot \boldsymbol{\mu}^B}{R^3}
$$

Each term factorizes in A and B operators **!**

The first order energy is

$$E_0^{(1)} = \langle\ \Phi_0^{(0)}\ |\ H^{(1)}\ |\ \Phi_0^{(0)}\ \rangle = \langle\ \Phi_0^A \Phi_0^B\ |\ H^{(1)}\ |\ \Phi_0^A \Phi_0^B\ \rangle$$

The first order energy is

$$E_0^{(1)} = \langle\ \Phi_0^{(0)}\ |\ H^{(1)}\ |\ \Phi_0^{(0)}\ \rangle = \langle\ \Phi_0^A \Phi_0^B\ |\ H^{(1)}\ |\ \Phi_0^A \Phi_0^B\ \rangle$$

With the multipole expansion of $H^{(1)}$ one can separate integration over the coordinates (x_i, y_i, z_i) and (x_j, y_j, z_j) of the particles $i \in A$ and $j \in B$ and obtain

$$E_0^{(1)} = \frac{q^A q^B}{R} + \frac{\langle\ \mu_z^A\ \rangle q^B}{R^2} - \frac{q^A \langle\ \mu_z^B\ \rangle}{R^2} + \frac{\langle\ \boldsymbol{\mu}^A\ \rangle \cdot \boldsymbol{T} \cdot \langle\ \boldsymbol{\mu}^B\ \rangle}{R^3}$$

The first order energy is

$$E_0^{(1)} = \langle\ \Phi_0^{(0)}\ |\ H^{(1)}\ |\ \Phi_0^{(0)}\ \rangle = \langle\ \Phi_0^A \Phi_0^B\ |\ H^{(1)}\ |\ \Phi_0^A \Phi_0^B\ \rangle$$

With the multipole expansion of $H^{(1)}$ one can separate integration over the coordinates (x_i, y_i, z_i) and (x_j, y_j, z_j) of the particles $i \in A$ and $j \in B$ and obtain

$$E_0^{(1)} = \frac{q^A q^B}{R} + \frac{\langle\ \mu_z^A\ \rangle q^B}{R^2} - \frac{q^A \langle\ \mu_z^B\ \rangle}{R^2} + \frac{\langle\ \boldsymbol{\mu}^A\ \rangle \cdot \boldsymbol{T} \cdot \langle\ \boldsymbol{\mu}^B\ \rangle}{R^3}$$

the same as in classical electrostatics, with the permanent multipole moments $\langle\ \boldsymbol{\mu}^A\ \rangle = \langle\ \Phi_0^A\ |\ \boldsymbol{\mu}^A\ |\ \Phi_0^A\ \rangle$ and $\langle\ \boldsymbol{\mu}^B\ \rangle = \langle\ \Phi_0^B\ |\ \boldsymbol{\mu}^B\ |\ \Phi_0^B\ \rangle$

The second order energy is

$$E_0^{(2)} = \sum_{K \neq 0} \frac{\langle \, \Phi_0^{(0)} \mid H^{(1)} \mid \Phi_K^{(0)} \, \rangle \langle \, \Phi_K^{(0)} \mid H^{(1)} \mid \Phi_0^{(0)} \, \rangle}{E_0^{(0)} - E_K^{(0)}}$$

The index K that labels the excited states of the system is a composite index $K = (k_1, k_2)$. The summation over $K \neq 0$ can be split into three sums, with

$k_1 \neq 0, \;\; k_2 = 0$	Molecule A excited
$k_1 = 0, \;\; k_2 \neq 0$	Molecule B excited
$k_1 \neq 0, \;\; k_2 \neq 0$	Both molecules excited

The first term of $E_0^{(2)}$ is

$$\sum_{k_1 \neq 0} \frac{\langle\, \Phi_0^A \Phi_0^B \mid H^{(1)} \mid \Phi_{k_1}^A \Phi_0^B \,\rangle \langle\, \Phi_{k_1}^A \Phi_0^B \mid H^{(1)} \mid \Phi_0^A \Phi_0^B \,\rangle}{E_0^A - E_{k_1}^A}$$

The first term of $E_0^{(2)}$ is

$$\sum_{k_1\neq 0} \frac{\langle\, \Phi_0^A \Phi_0^B \mid H^{(1)} \mid \Phi_{k_1}^A \Phi_0^B \,\rangle \langle\, \Phi_{k_1}^A \Phi_0^B \mid H^{(1)} \mid \Phi_0^A \Phi_0^B \,\rangle}{E_0^A - E_{k_1}^A}$$

The operator $H(1)$ is term-by-term factorizable and the integrals in this expression can be separated. For example

$$\begin{aligned}\langle\, \Phi_0^A \Phi_0^B \mid \frac{\mu_z^A \mu_z^B}{R^3} \mid \Phi_{k_1}^A \Phi_0^B \,\rangle &= \frac{\langle\, \Phi_0^A \mid \mu_z^A \mid \Phi_{k_1}^A \,\rangle \langle\, \Phi_0^B \mid \mu_z^B \mid \Phi_0^B \,\rangle}{R^3} \\ &= \frac{\langle\, \Phi_0^A \mid \mu_z^A \mid \Phi_{k_1}^A \,\rangle \langle\, \mu_z^B \,\rangle}{R^3}\end{aligned}$$

Furthermore, one may use the orthogonality relation $\langle\, \Phi_0^A \mid \Phi_{k_1}^A \,\rangle = 0$.

The transition dipole moments $\langle\, \Phi_0^A \mid \mu_z^A \mid \Phi_{k_1}^A \,\rangle$, with the summation over $k_1 \neq 0$, occur in the formula for the polarizability α_{zz}^A.

The transition dipole moments $\langle\, \Phi_0^A \mid \mu_z^A \mid \Phi_{k_1}^A \,\rangle$, with the summation over $k_1 \neq 0$, occur in the formula for the polarizability α_{zz}^A.

If one assumes that the polarizability is isotropic, $\alpha_{xx}^A = \alpha_{yy}^A = \alpha_{zz}^A = \alpha^A$, one finds for the first term

$$\begin{aligned} E_0^{(2)}(\mathrm{pol.}\, A) &= -\frac{\alpha^A (q^B)^2}{2R^4} + \frac{2\alpha^A q^B \langle\, \mu_z^B \,\rangle}{R^5} \\ &\quad - \frac{\alpha^A (\langle\, \mu_x^B \,\rangle^2 + \langle\, \mu_y^B \,\rangle^2 + 4\langle\, \mu_z^B \,\rangle^2)}{2R^6} \end{aligned}$$

Also this results agree with classical electrostatics. The electric field of the point charge q^B at the center of molecule A is

$$\boldsymbol{F} = (F_x, F_y, F_z) = \left(0, 0, -\frac{q^B}{R^2}\right)$$

and the electric field of the permanent dipole moment $\langle\ \boldsymbol{\mu}^B\ \rangle$ is

$$\boldsymbol{F} = \left(-\frac{\langle\ \mu_x^B\ \rangle}{R^3}, -\frac{\langle\ \mu_y^B\ \rangle}{R^3}, \frac{2\langle\ \mu_z^B\ \rangle}{R^3}\right)$$

The second order interaction energy $E_0^{(2)}(\mathrm{pol.}\,A)$ is simply the polarization energy $-\frac{1}{2}\alpha^A F^2$ of molecule A in the electric field of the charge and dipole of molecule B.

Analogously, we find for the second term, which includes a summation over the excited states k_2 of molecule B

$$\begin{aligned} E_0^{(2)}(\text{pol.}\,B) \;&=\; -\frac{(q^A)^2\alpha^B}{2R^4} - \frac{2q^A\langle\, \mu_z^A \,\rangle\alpha^B}{R^5} \\ &\quad -\frac{(\langle\, \mu_x^A \,\rangle^2 + \langle\, \mu_y^A \,\rangle^2 + 4\langle\, \mu_z^A \,\rangle^2)\alpha^B}{2R^6} \end{aligned}$$

This is the classical energy of polarization of molecule B in the field of A.

The third term contains the summation over the excited states of both molecules. All interaction terms with the charges q^A and q^B cancel, because of the orthogonality relation $\langle\ \Phi_0^A \mid \Phi_{k_1}^A\ \rangle = 0$. Only the dipole-dipole term of $H^{(1)}$ is left and we obtain

$$\begin{aligned}
&E_0^{(2)}(\mathrm{disp}) \\
&\quad = \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \frac{\langle\ \Phi_0^A \Phi_0^B \mid H^{(1)} \mid \Phi_{k_1}^A \Phi_{k_2}^B\ \rangle \langle\ \Phi_{k_1}^A \Phi_{k_2}^B \mid H^{(1)} \mid \Phi_0^A \Phi_0^B\ \rangle}{(E_0^A - E_{k_1}^A) + (E_0^B - E_{k_2}^B)} \\
&\quad = -R^{-6} \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \frac{\left| \langle\ \Phi_0^A \mid \boldsymbol{\mu}^A \mid \Phi_{k_1}^A\ \rangle \cdot \boldsymbol{T} \cdot \langle\ \Phi_0^B \mid \boldsymbol{\mu}^B \mid \Phi_{k_2}^B\ \rangle \right|^2}{(E_{k_1}^A - E_0^A) + (E_{k_2}^B - E_0^B)}
\end{aligned}$$

This term, the dispersion energy, has no classical equivalent; it is purely quantum mechanical.

It is proportional to R^{-6}.

This term, the dispersion energy, has no classical equivalent; it is purely quantum mechanical.
It is proportional to R^{-6}.

It can be easily proved that each of the three second order terms is negative. Therefore, the induction and dispersion energies are always attractive.

This term, the dispersion energy, has no classical equivalent; it is purely quantum mechanical.
It is proportional to R^{-6}.

It can be easily proved that each of the three second order terms is negative. Therefore, the induction and dispersion energies are always attractive.

For neutral, non-polar molecules the charges q^A, q^B and permanent dipole moments $\langle \boldsymbol{\mu}^A \rangle, \langle \boldsymbol{\mu}^B \rangle$ are zero, and the dispersion energy is the only second order interaction.

Terms with higher powers of R^{-1} occur as well. They originate from the quadrupole and higher multipole moments that we neglected.

Terms with higher powers of R^{-1} occur as well. They originate from the quadrupole and higher multipole moments that we neglected.

An approximate formula, due to London, that is often used to estimate the dispersion energy is

$$E_0^{(2)}(\mathrm{disp}) \approx -\frac{3\alpha^A\alpha^B}{2R^6}\frac{I^AI^B}{I^A+I^B}$$

This formula is found if one assumes that all the excitation energies $E_{k_1}^A - E_0^A$ and $E_{k_2}^B - E_0^B$ are the same, and are equal to the ionization energies I^A and I^B.

Summary of long range interactions

The interactions between two molecules A and B can be derived by means of QM perturbation theory.

Summary of long range interactions

The interactions between two molecules A and B can be derived by means of QM perturbation theory.

The first order energy equals the classical electrostatic (Coulomb) interaction energy between the charges and dipole moments of the molecules. It may be attractive or repulsive, depending on the (positive or negative) charges and on the orientations of the dipole moments. The dipolar terms average out when the dipoles are freely rotating.

The second order energy consists of three contributions. The first two terms correspond to the classical polarization energies of the molecules in each other's electric fields. The third term is purely QM. All the three contributions are attractive. They start with R^{-4} terms when the molecules have charges and with R^{-6} terms when they are neutral. The dispersion energy, with the leading term proportional to R^{-6}, occurs also for neutral molecules with no permanent dipole moments.

The second order energy consists of three contributions. The first two terms correspond to the classical polarization energies of the molecules in each other's electric fields. The third term is purely QM. All the three contributions are attractive. They start with R^{-4} terms when the molecules have charges and with R^{-6} terms when they are neutral. The dispersion energy, with the leading term proportional to R^{-6}, occurs also for neutral molecules with no permanent dipole moments.

All of these terms can be calculated when the wave functions $\Phi^A_{k_1}, \Phi^B_{k_2}$ and energies $E^A_{k_1}, E^B_{k_2}$ of the free molecules A and B are known, but one should somehow approximate the infinite summations over excited states k_1 and k_2 that occur in the second order expressions.

Interactions in the overlap region

Heitler and London (Valence Bond) wave functions for H$_2$

$$1s_A(\boldsymbol{r}_1)1s_B(\boldsymbol{r}_2) \pm 1s_B(\boldsymbol{r}_1)1s_A(\boldsymbol{r}_2)$$

with the plus sign for the singlet spin ($S = 0$) function

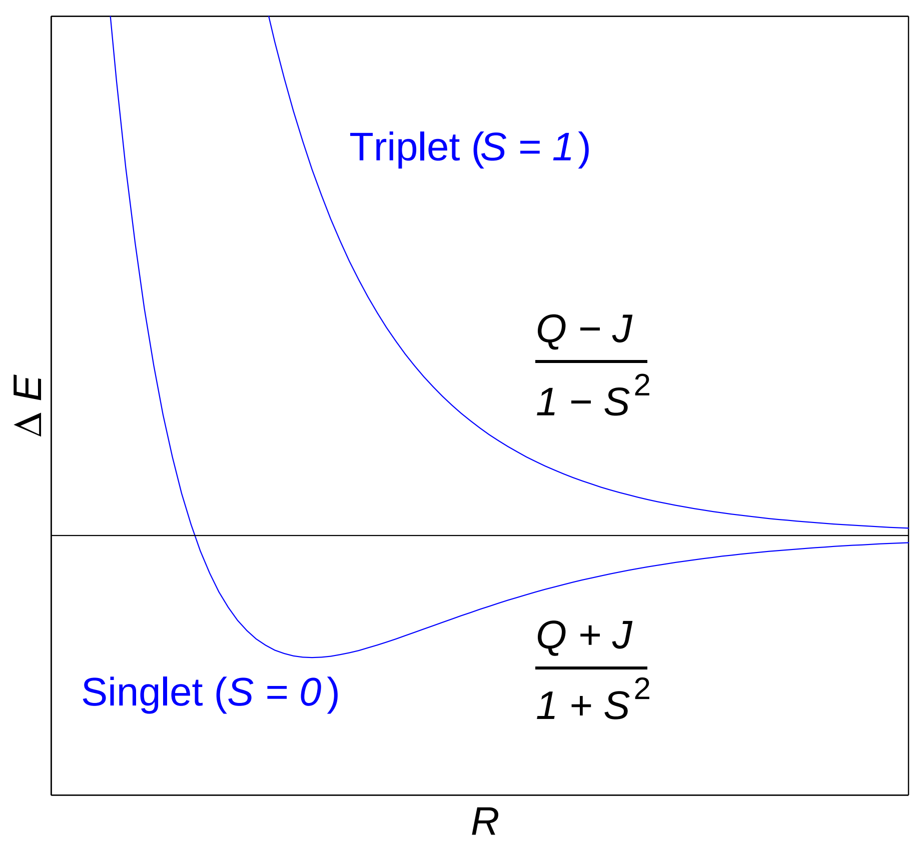
$$\alpha(1)\beta(2) - \beta(1)\alpha(2)$$

and the minus sign for the triplet spin ($S = 1$) functions

$$\begin{gathered} \alpha(1)\alpha(2) \\ \alpha(1)\beta(2) + \beta(1)\alpha(2) \\ \beta(1)\beta(2) \end{gathered}$$

The total electronic wave function is antisymmetric (Pauli)

Interaction energy $\Delta E(R) = E_{\mathrm{H}_2} - 2E_{\mathrm{H}}$



$Q(R)$ = “Coulomb integral”

$J(R)$ = “exchange integral”

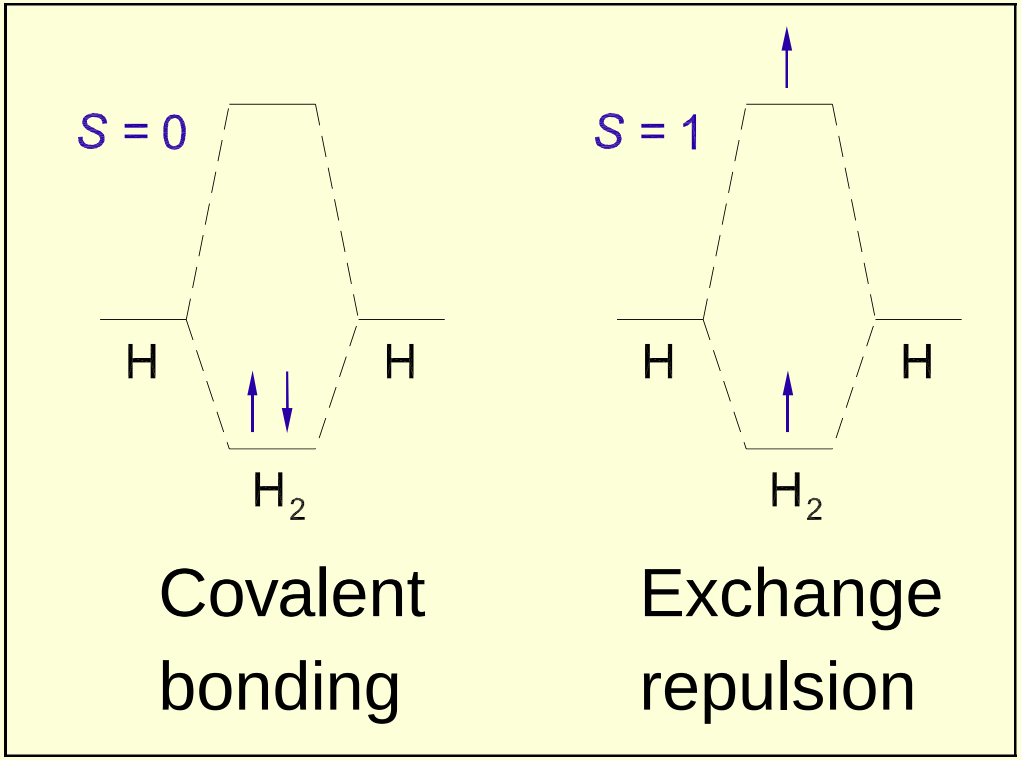
$S(R)$ = $\langle\, 1s_A \,|\, 1s_B \,\rangle$
= overlap integral

Interaction is dominated by the exchange integral $J(R)$, which is negative, so that the exchange interaction is attractive (covalent bonding) in the singlet state and repulsive in the triplet state.

Interaction is dominated by the exchange integral $J(R)$, which is negative, so that the exchange interaction is attractive (covalent bonding) in the singlet state and repulsive in the triplet state.

For He_2 there is only one (singlet) state and the interaction energy $\Delta E(R)$ is purely repulsive: exchange (or Pauli) repulsion or steric hindrance.

Molecular orbital picture

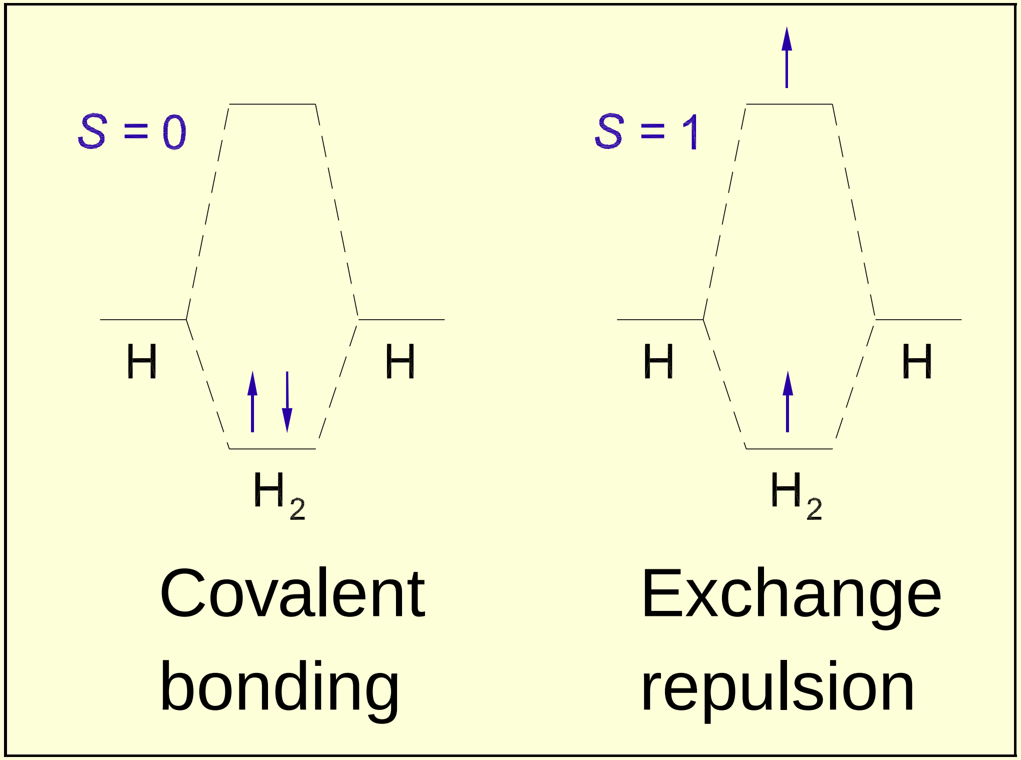


Covalent bonding

Exchange repulsion

H–H interaction

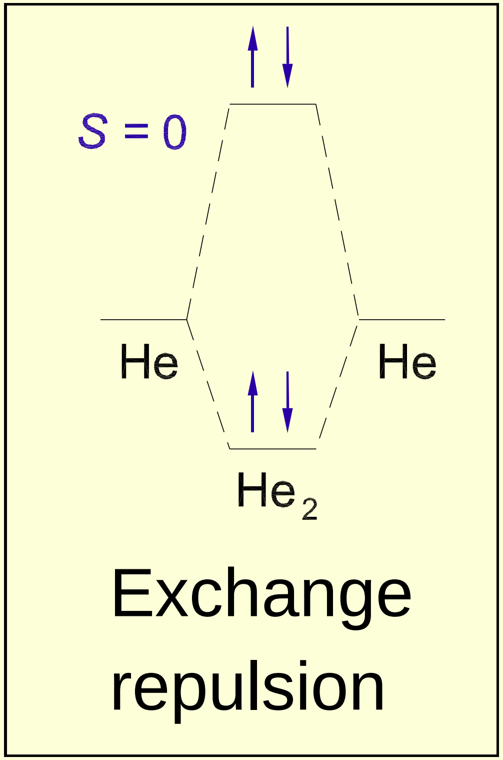
Molecular orbital picture



Covalent bonding

Exchange repulsion

H–H interaction



Exchange repulsion

He–He interaction

Most stable molecules are closed-shell systems and the exchange energy between them is always repulsive. It depends on the overlap between the wave functions of A and B and decays exponentially with the distance R.

Most stable molecules are closed-shell systems and the exchange energy between them is always repulsive. It depends on the overlap between the wave functions of A and B and decays exponentially with the distance R.

In combination with attractive long range interactions (proportional to R^{-n}) this gives rise to a minimum in $\Delta E(R)$. This, so-called, *non-covalent bonding* is much weaker than covalent bonding, except when A and B are (atomic or molecular) ions with opposite charges (cf. $\mathrm{Na}^{+}\mathrm{Cl}^{-}$).

Most stable molecules are closed-shell systems and the exchange energy between them is always repulsive. It depends on the overlap between the wave functions of A and B and decays exponentially with the distance R.

In combination with attractive long range interactions (proportional to R^{-n}) this gives rise to a minimum in $\Delta E(R)$. This, so-called, *non-covalent bonding* is much weaker than covalent bonding, except when A and B are (atomic or molecular) ions with opposite charges (cf. $\mathrm{Na}^{+}\mathrm{Cl}^{-}$).

Binding (merely by the attractive dispersion energy) is weakest when both molecules are neutral and non-polar: pure Van der Waals interactions.

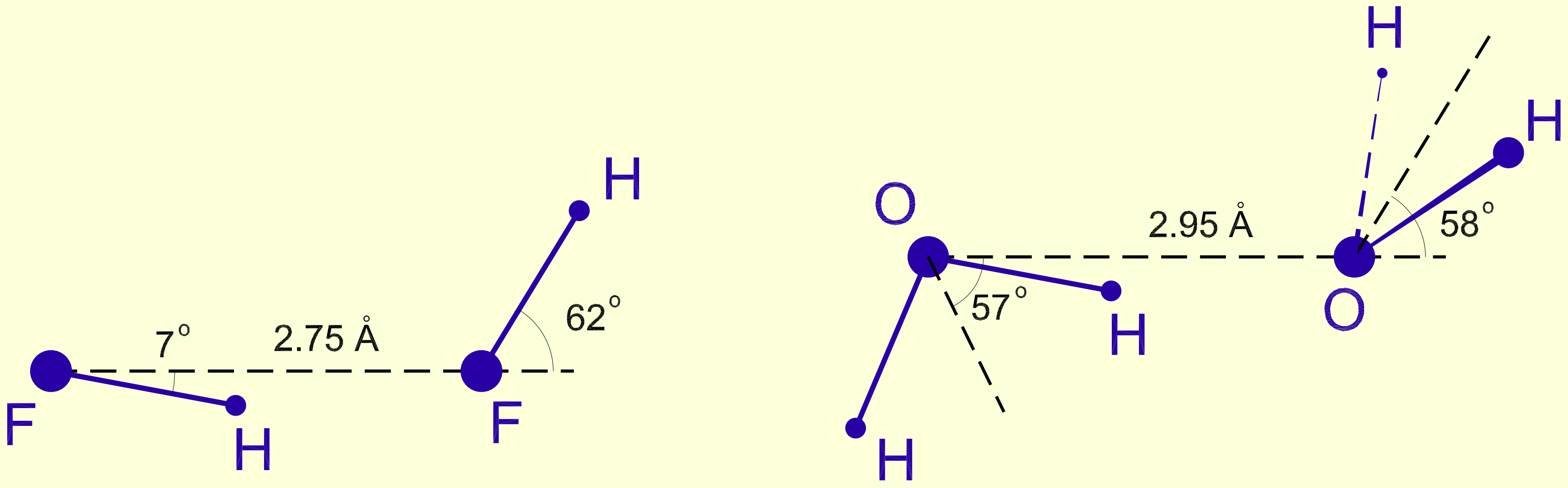
A special type of interactions between polar molecules is *hydrogen bonding*

$$\mathrm{X{-}H}\cdots\mathrm{Y}$$

The binding mainly originates from electrostatic (dipolar and quadrupolar) interactions and the corresponding induction terms and is strongly directional.

No special (HOMO-LUMO, charge-transfer, or weak covalent bonding) interactions are needed **!**

Exercise:



Compute the equilibrium angles of HF–HF at $R = 2.75$ Å and H_2O–H_2O at $R = 2.95$ Å from the dipolar and quadrupolar interactions only.

Non-covalent interactions and hydrogen bonding, in particular, are very important in biology. Alpha helices and beta sheets in proteins are stabilized by intra- and inter-molecular hydrogen bonds, and the double stranded structure of DNA is held together by hydrogen bonds between the base pairs.

Non-covalent interactions and hydrogen bonding, in particular, are very important in biology. Alpha helices and beta sheets in proteins are stabilized by intra- and inter-molecular hydrogen bonds, and the double stranded structure of DNA is held together by hydrogen bonds between the base pairs.

It is essential that a hierarchy of interactions exists with binding energies varying over several orders of magnitude. Interactions in biological systems must be sufficiently strong to maintain stable structures, but not so strong that they prevent rearrangement processes (DNA replication, for instance).

Intermolecular potentials (or force fields)

Concept based on Born-Oppenheimer approximation (separation of electronic and nuclear motion)

Step 1: Solve electronic Schrödinger equation

$$H_{\rm el}(\boldsymbol{r}_{\rm el};\boldsymbol{R})\Psi(\boldsymbol{r}_{\rm el};\boldsymbol{R}) = E(\boldsymbol{R})\Psi(\boldsymbol{r}_{\rm el};\boldsymbol{R})$$

for clamped nuclei at positions $\boldsymbol{R}$. Yields energy $E(\boldsymbol{R})$.

Step 2: Use $E(\boldsymbol{R})$ as potential energy in solving Schrödinger equation for nuclear motion. Yields bound levels of Van der Waals complexes and scattering states (cross sections).

Intermolecular potential of a many-body system

$$V = \sum_{A<B} V_{AB} + \sum_{A<B<C} V_{ABC} + \dots$$

pair three-body

Intermolecular potential of a many-body system

$$V = \underbrace{\sum_{A<B} V_{AB}}_{\text{pair}} + \underbrace{\sum_{A<B<C} V_{ABC}}_{\text{three-body}} + \dots$$

Pair potential, in space-fixed (SF) coordinates

$$V_{AB} = V\left(\boldsymbol{R}_{AB}, \boldsymbol{\Omega}_A, \boldsymbol{\Omega}_B, \boldsymbol{q}_A, \boldsymbol{q}_B\right)$$

$$\left.\begin{array}{l}\text{Euler angles } \boldsymbol{\Omega}_X = (\alpha_X, \beta_X, \gamma_X) \\ \text{internal coordinates } \boldsymbol{q}_X\end{array}\right\} \text{for } X = A, B$$

Three angles, the two polar angles of $\boldsymbol{R}_{AB}$ and one of the Euler angles α_X (say α_A), can be chosen as overall rotation angles of the complex A–B.

The pair potential in body-fixed (BF) coordinates is

$$V_{AB} = V\left(R_{AB}, \alpha_B - \alpha_A, \beta_A, \beta_B, \gamma_A, \gamma_B, \boldsymbol{q}_A, \boldsymbol{q}_B\right)$$

The internal coordinates $\boldsymbol{q}_A, \boldsymbol{q}_B$ are often frozen (rigid molecules). This is justified by a Born-Oppenheimer-like separation between the fast intramolecular vibrations (coordinates $\boldsymbol{q}_A, \boldsymbol{q}_B$) and the much slower VRT motions (vibrations, hindered rotations, tunneling) of the whole molecules A and B in the complex.

Ab initio calculation of intermolecular potentials

- Supermolecule calculations
- Symmetry-adapted perturbation theory (SAPT)

Supermolecule calculations

$$\Delta E = E_{AB} - E_A - E_B$$

Requirements:

1. Include electron correlation, intra- and inter-molecular (dispersion energy = intermolecular correlation)
2. Choose good basis, with diffuse orbitals (and “bond functions”) especially to converge the dispersion energy
3. Size consistency. Currently best method: CCSD(T)
4. Correct for basis set superposition error (BSSE) by computing E_A and E_B in dimer basis

Symmetry-adapted perturbation theory (SAPT)

Combine perturbation theory with antisymmetrization $\mathcal{A}$ (Pauli) to include short-range exchange effects.

Symmetry-adapted perturbation theory (SAPT)

Combine perturbation theory with antisymmetrization $\mathcal{A}$ (Pauli) to include short-range exchange effects.

Advantages:

1. ΔE calculated directly.
2. Contributions (electrostatic, induction, dispersion, exchange) computed individually. Useful in analytic fits of potential surface.

Symmetry-adapted perturbation theory (SAPT)

Combine perturbation theory with antisymmetrization $\mathcal{A}$ (Pauli) to include short-range exchange effects.

Advantages:

1. ΔE calculated directly.
2. Contributions (electrostatic, induction, dispersion, exchange) computed individually. Useful in analytic fits of potential surface.

Advantage of supermolecule method:

Easy, use any black-box molecular electronic structure program

Problems in SAPT:

1. Pauli: $\mathcal{A}H = H\mathcal{A}$.
   Antisymmetrizer commutes with total Hamiltonian $H = H^{(0)} + H^{(1)}$, but not with $H^{(0)}$ and $H^{(1)}$ separately.
   Has led to different definitions of second (and higher) order energies.
2. Free monomer wavefunctions $\Phi_{k_1}^{A}$ and $\Phi_{k_2}^{B}$ not exactly known. Use Hartree-Fock wave functions and apply double perturbation theory to include intra-molecular correlation, or use CCSD wave functions of monomers.

Problems in SAPT:

1. Pauli: $\mathcal{A}H = H\mathcal{A}$.
   Antisymmetrizer commutes with total Hamiltonian $H = H^{(0)} + H^{(1)}$, but not with $H^{(0)}$ and $H^{(1)}$ separately. Has led to different definitions of second (and higher) order energies.
2. Free monomer wavefunctions $\Phi^{A}_{k_1}$ and $\Phi^{B}_{k_2}$ not exactly known. Use Hartree-Fock wave functions and apply double perturbation theory to include intra-molecular correlation, or use CCSD wave functions of monomers.

Program packages:

- SAPT2 for pair potentials
- SAPT3 for 3-body interactions