

Equations of state

Ideal gas

$$pV = kT$$

Non-ideal gas (Van der Waals)

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

repulsion \Rightarrow b (eigenvolume)

attraction \Rightarrow a (reduced pressure)

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

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

with

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

$\Delta E(R)$ is the interaction energy between two atoms/molecules as function of their distance R

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⇒ covalent bonding for singlet H_2 ($S = 0$)

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1927 / 1930

Wang, London: QM ⇒ dispersion forces (attractive)

QM derivation of intermolecular forces

correspondence with classical electrostatics

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Intermezzo:

(Time-independent) perturbation theory

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

Perturbation theory \Rightarrow Approximate solutions E_k and Φ_k

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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

$$E_k(\lambda) = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots$$

$$\Phi_k(\lambda) = \Phi_k^{(0)} + \lambda \Phi_k^{(1)} + \lambda^2 \Phi_k^{(2)} + \dots$$

Expand

$$E_k(\lambda) = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \dots$$

$$\Phi_k(\lambda) = \Phi_k^{(0)} + \lambda \Phi_k^{(1)} + \lambda^2 \Phi_k^{(2)} + \dots$$

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

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

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

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

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

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

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

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

The second order energy may also be written as

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

Molecule in electric field

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

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

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

and perturbation

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

Multipole (Taylor) expansion

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

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

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

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Perturbation operator

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

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

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

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

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Energy of permanent dipole $\langle \boldsymbol{\mu} \rangle$ in field \mathbf{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., $\mathbf{F}_0 = (0, 0, F_0)$ and $H^{(1)} = -\mu_z F_0$

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

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

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

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

$$\begin{aligned} & \langle \Phi_0^{(0)} + \Phi_0^{(1)} | \mu_z | \Phi_0^{(0)} + \Phi_0^{(1)} \rangle = \\ & \langle \Phi_0^{(0)} | \mu_z | \Phi_0^{(0)} \rangle + 2 \langle \Phi_0^{(0)} | \mu_z | \Phi_0^{(1)} \rangle + \langle \Phi_0^{(1)} | \mu_z | \Phi_0^{(1)} \rangle \end{aligned}$$

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

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

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

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

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For arbitrary molecules the direction of the induced dipole moment μ_{ind} is not parallel to F_0 . The polarizability α is a second rank tensor with non-zero elements α_{xy} , etc.

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For isotropic systems (atoms, freely rotating molecules) α 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 $j \in B$.

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

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

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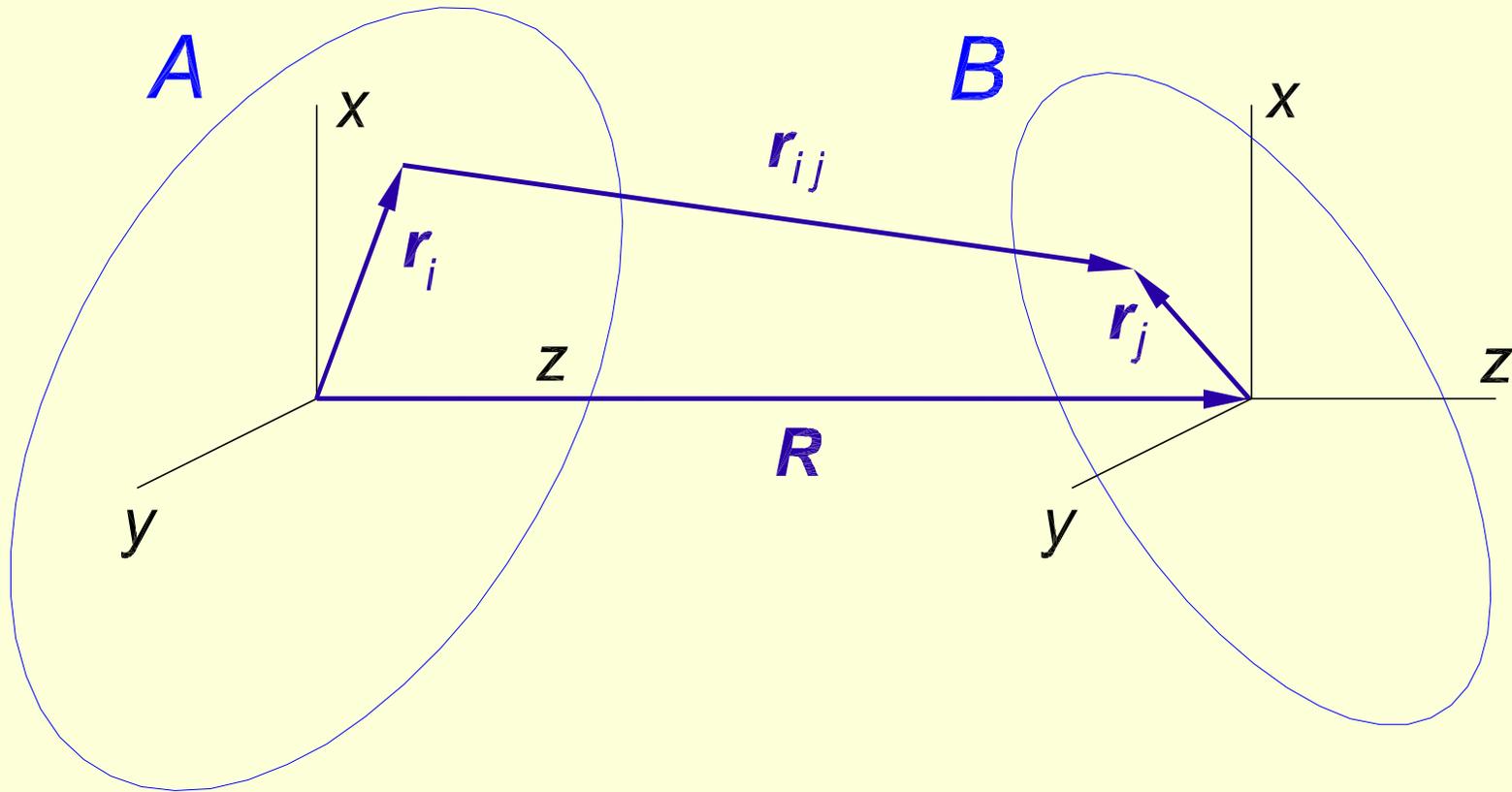
$$H^{(1)} = \sum_{i \in A} \sum_{j \in B} \frac{q_i q_j}{r_{ij}}$$

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

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

of molecule B .

Multipole expansion of the interaction operator



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

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

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

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

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

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 $q^A = \sum_{i \in A} q_i$ $q^B = \sum_{j \in B} q_j$

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

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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

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

with the interaction tensor

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

This tensor can also be expressed in more general coordinates.

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

$$\begin{aligned}H^A \Phi_{k_1}^A &= E_{k_1}^A \Phi_{k_1}^A \\H^B \Phi_{k_2}^B &= E_{k_2}^B \Phi_{k_2}^B\end{aligned}$$

and of the unperturbed problem

$$H^{(0)} \Phi_K^{(0)} = E_K^{(0)} \Phi_K^{(0)}$$

with $\Phi_K^{(0)} = \Phi_{k_1}^A \Phi_{k_2}^B$ and eigenvalues $E_K^{(0)} = E_{k_1}^A + E_{k_2}^B$

Proof

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

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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

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

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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

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

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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

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

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

$$k_1 \neq 0, \quad k_2 = 0$$

Molecule A excited

$$k_1 = 0, \quad k_2 \neq 0$$

Molecule B excited

$$k_1 \neq 0, \quad k_2 \neq 0$$

Both molecules excited

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

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

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

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

Furthermore, one may use the orthogonality relation

$$\langle \Phi_0^A | \Phi_{k_1}^A \rangle = 0.$$

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

The transition dipole moments $\langle \Phi_0^A | \mu_z^A | \Phi_{k_1}^A \rangle$, 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

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

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

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

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

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

The second order interaction energy $E_0^{(2)}$ (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

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

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 $\langle \Phi_0^A | \Phi_{k_1}^A \rangle = 0$. Only the dipole-dipole term of $H^{(1)}$ is left and we obtain

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

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

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For neutral, non-polar molecules the charges q^A, q^B and permanent dipole moments $\langle \mu^A \rangle, \langle \mu^B \rangle$ 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.

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

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

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.

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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.

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All of these terms can be calculated when the wave functions $\Phi_{k_1}^A$, $\Phi_{k_2}^B$ and energies $E_{k_1}^A$, $E_{k_2}^B$ 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 H₂

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

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

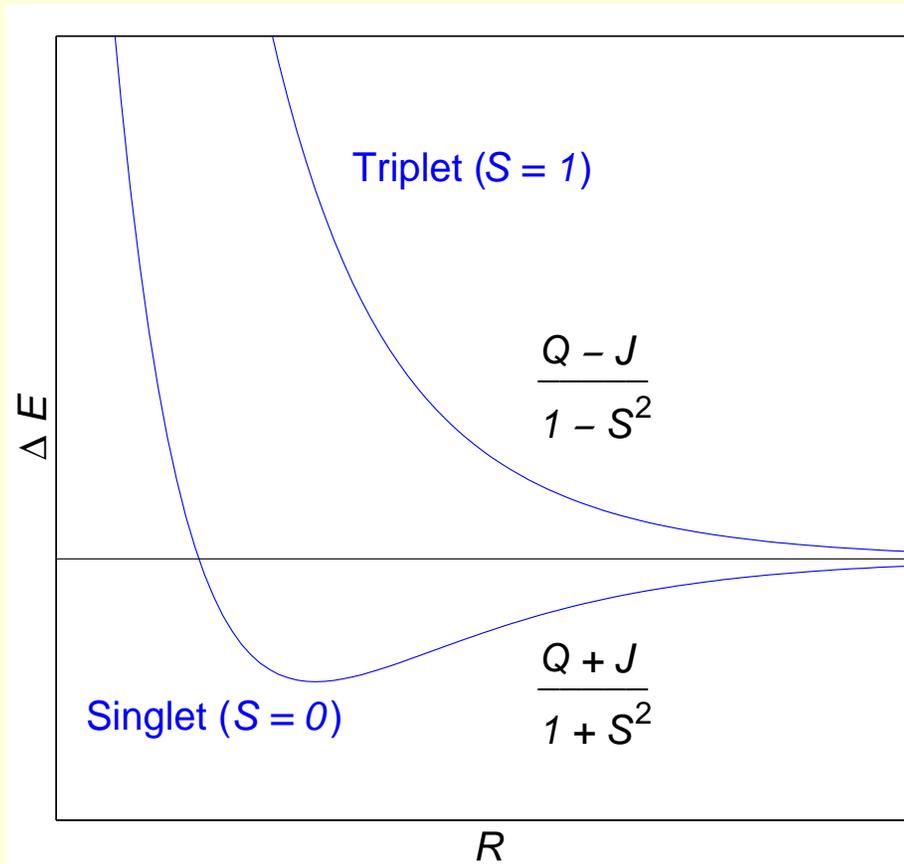
$$\alpha(1)\alpha(2)$$

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

$$\beta(1)\beta(2)$$

The total electronic wave function is antisymmetric (Pauli)

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



$Q(R)$ = “Coulomb integral”

$J(R)$ = “exchange integral”

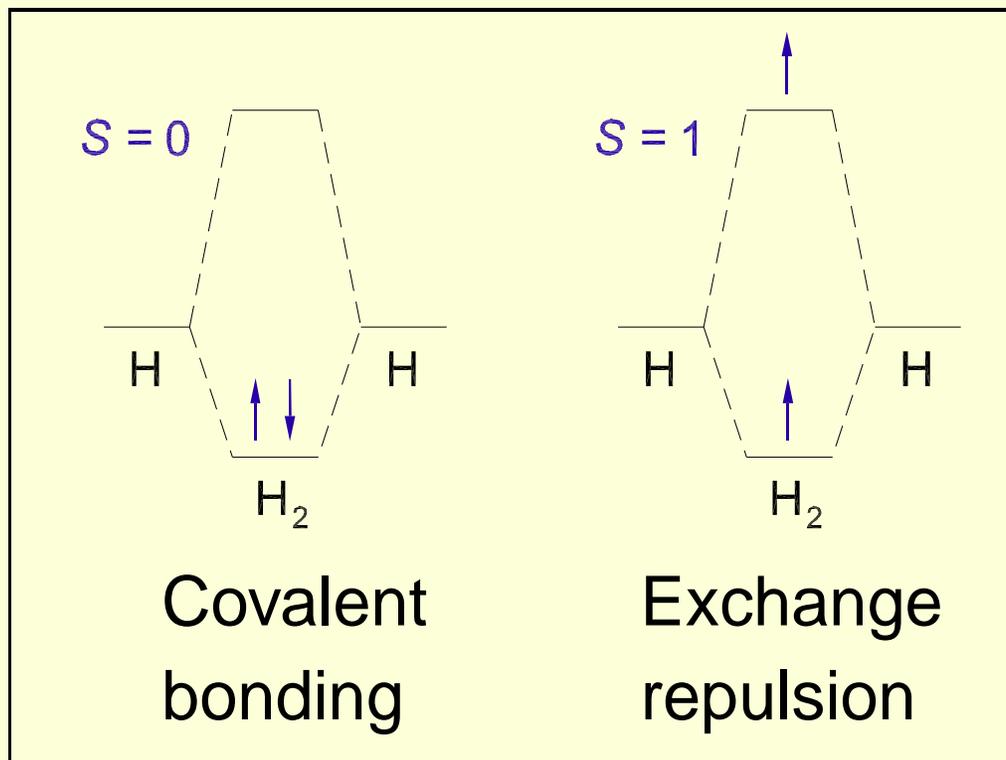
$S(R)$ = $\langle 1s_A | 1s_B \rangle$
= overlap integral

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.

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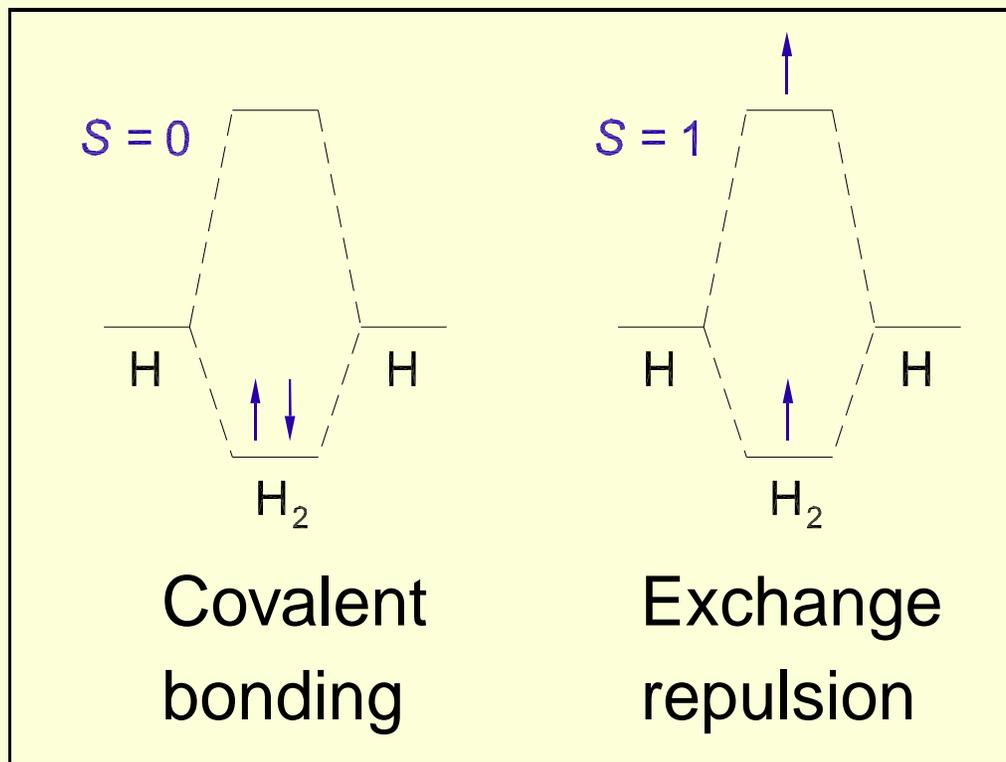
For He_2 there is only one (singlet) state and the interaction energy $\Delta E(R)$ is purely repulsive: exchange (or Pauli) repulsion or steric hindrance.

Molecular orbital picture

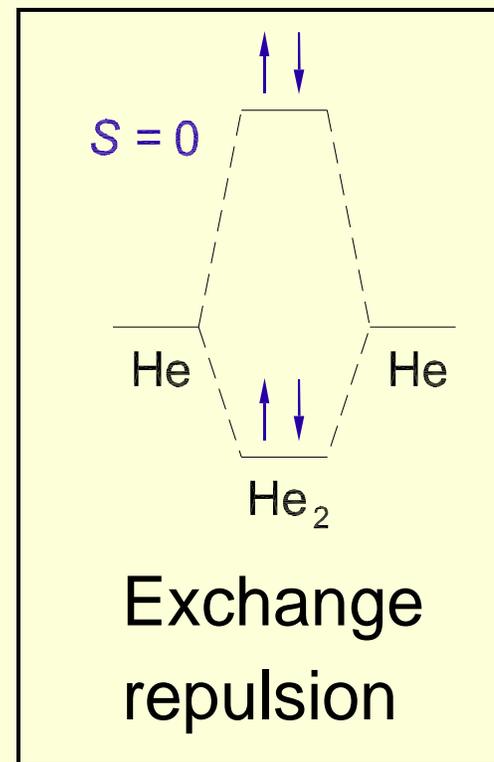


H–H interaction

Molecular orbital picture



H–H interaction



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 .

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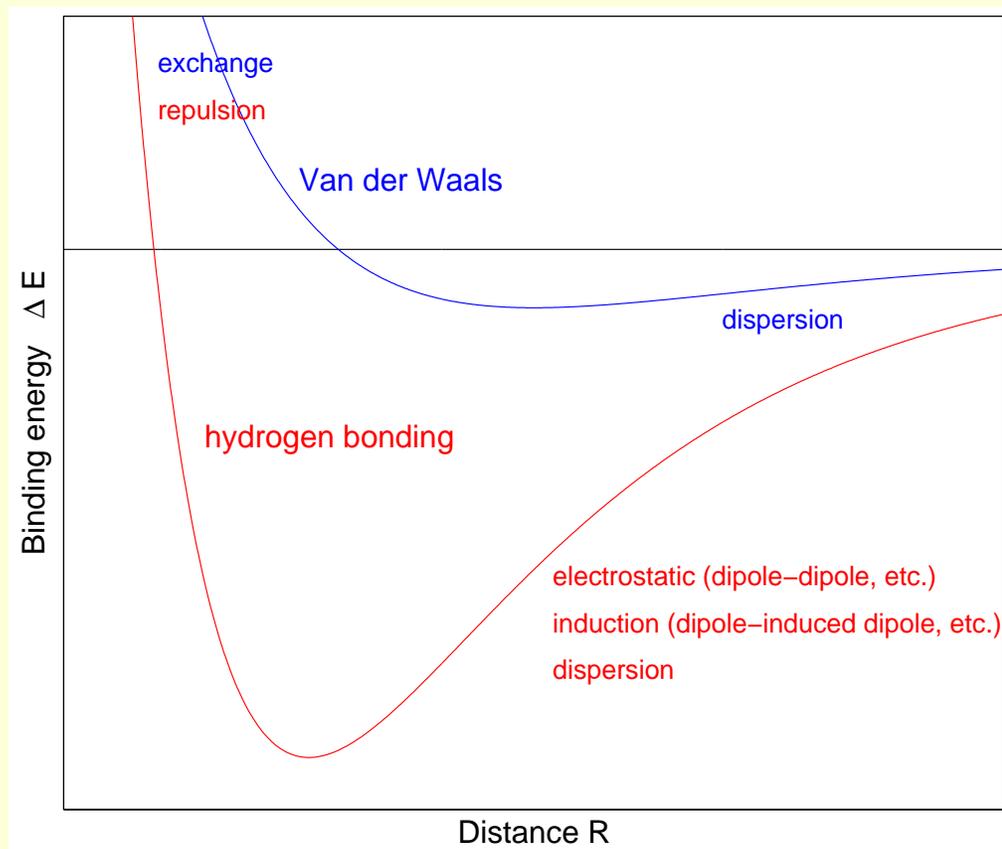
In combination with attractive long range interactions (proportional to R^{-n}) this gives rise to a minimum in $\Delta E(R)$. This, so-called, *non-covalent bonding* is much weaker than covalent bonding, except when A and B are (atomic or molecular) ions with opposite charges (cf. Na^+Cl^-).

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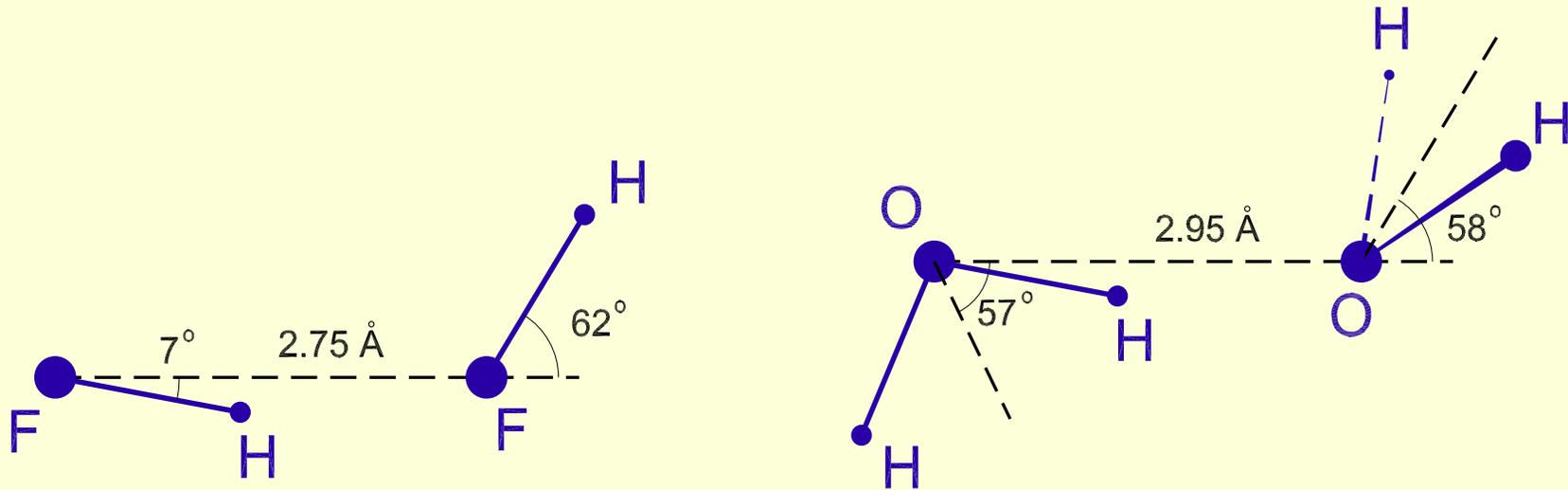
Binding (merely by the attractive dispersion energy) is weakest when both molecules are neutral and non-polar: pure Van der Waals interactions.

A special type of interactions between polar molecules is
hydrogen bonding: $X-H \cdots Y$



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

Exercise:



Compute the equilibrium angles of HF–HF at $R = 2.75 \text{ \AA}$ and H₂O–H₂O at $R = 2.95 \text{ \AA}$ 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.

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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).