Noncovalent interactions between molecules

and

spectra of weakly bound molecular clusters

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Outline:

- Preamble: Born-Oppenheimer approximation

- What are non-covalent interactions?
  Quantum mechanical derivation

- How to compute intermolecular force fields *ab initio*?

- How to test intermolecular force fields?
  Van der Waals molecules, spectra

- Illustration: *ab initio* force field for water, applications

- Molecular collisions, scattering resonances

Useful concepts:

- Molecular force fields (MM calculations)
- Interatomic / intermolecular forces (potential energy surfaces)
- Forces on atoms in solids
- Equilibrium structure, force constants of a molecule
- Chemical reaction paths (from QM calculations)

Exist only in the Born-Oppenheimer approximation

Born-Oppenheimer (adiabatic) approximation

Step 1:

Solve electronic Schrödinger equation

$$H_{\mathsf{e}}\,\phi(\mathbf{r};\mathbf{R}) = E_{\mathsf{e}}(\mathbf{R})\,\phi(\mathbf{r};\mathbf{R})$$

for nuclei fixed at positions $\mathbf{R}$.

Involves neglect of nuclear kinetic energy T_{n}.

Step 2:

Solve nuclear Schrödinger equation

$$[T_{\mathsf{n}} + E_{\mathsf{e}}(\mathbf{R})]\,\chi(\mathbf{R}) = E\chi(\mathbf{R})$$

with potential energy surface $E_{\mathsf{e}}(\mathbf{R})$

⇒ vibrations, rotations, (phonons, librations), chemical reaction dynamics, molecular collisions.

Alternative for step 2

Molecular dynamics (MD):

solve nuclear motions classically on potential surface $E_{\mathrm{e}}(\mathbf{R})$.

Derivation of the Born-Oppenheimer approximation

Exact (non-relativistic) Hamiltonian

$$H = T_{\mathrm{n}} + T_{\mathrm{e}} + V(\mathbf{r}, \mathbf{R})$$

with

$$T_{\mathrm{e}} = -\sum_i \frac{\hbar^2}{2m} \nabla_i^2 \qquad \text{and} \qquad T_{\mathrm{n}} = -\sum_A \frac{\hbar^2}{2M_A} \nabla_A^2$$

$$V(\mathbf{r}, \mathbf{R}) = \sum_{A>B} \frac{Z_A Z_B e^2}{|\mathbf{R}_A - \mathbf{R}_B|} - \sum_{i,A} \frac{Z_A e^2}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

Electronic Hamiltonian (with the nuclei fixed at positions $\mathbf{R}$)

$$H_{\mathrm{e}} = T_{\mathrm{e}} + V(\mathbf{r}, \mathbf{R})$$

The total Schrödinger equation reads

$$H\,\Psi(\mathbf{r},\mathbf{R}) = E\,\Psi(\mathbf{r},\mathbf{R})$$

Expand the total wave function

$$\Psi(\mathbf{r},\mathbf{R}) = \sum_k \phi_k(\mathbf{r};\mathbf{R})\chi_k(\mathbf{R})$$

in solutions $\phi_k(\mathbf{r};\mathbf{R})$ of the electronic Schrödinger equation

$$H_\mathsf{e}\,\phi_k(\mathbf{r};\mathbf{R}) = E_k(\mathbf{R})\,\phi_k(\mathbf{r};\mathbf{R})$$

and substitute it into the total Schrödinger equation.

Multiply by the function $\phi_{k'}(\mathbf{r};\mathbf{R})$ from the left and integrate over the electronic coordinates $\mathbf{r}$. The electronic Hamiltonian H_e is diagonal

$$\langle\phi_{k'}(\mathbf{r};\mathbf{R})|H_\mathsf{e}|\phi_k(\mathbf{r};\mathbf{R})\rangle_{(\mathbf{r})} = \delta_{k'k}E_k(\mathbf{R})$$

and the electronic wave functions are orthogonal

$$\langle\,\phi_{k'}(\mathbf{r};\mathbf{R})\,|\,\phi_k(\mathbf{r};\mathbf{R})\rangle_{(\mathbf{r})} = \delta_{k'k}$$

This yields a set of coupled eigenvalue equations for the nuclear wave functions

$$[\,T_{\mathsf{n}} + E_{k'}(\mathbf{R}) - E\,]\ \chi_{k'}(\mathbf{R}) = \sum_k [\,\mathbb{F}_{\mathsf{n}}]_{k'k}\ \chi_k(\mathbf{R})$$

Coupling between different electronic states k', k

$$[\,\mathbb{F}_{\mathsf{n}}]_{k'k}\,(\mathbf{R}) = \langle \phi_{k'}(\mathbf{r};\mathbf{R}) | T_{\mathsf{n}} |\, \phi_k(\mathbf{r};\mathbf{R}) \rangle_{(\mathbf{r})} - T_{\mathsf{n}}\,\delta_{k'k}$$

occurs through the nuclear kinetic energy operator T_{n}.

When this coupling is neglected one obtains the Born-Oppenheimer nuclear Schrödinger equation for electronic state k'

$$[T_{\mathsf{n}} + E_{k'}(\mathbf{R})]\,\chi_{k'}(\mathbf{R}) = E\,\chi_{k'}(\mathbf{R})$$

The (non-adiabatic) coupling terms are

$$[\mathbb{F}\mathsf{n}]_{k'k}\,(\mathbf{R}) = -\sum_A \frac{\hbar^2}{2M_A}\Big[2\langle\phi_{k'}|\big(\boldsymbol{\nabla}_A\phi_k\big)\rangle_{(\mathbf{r})}\cdot\boldsymbol{\nabla}_A + \langle\phi_{k'}|\big(\nabla_A^2\phi_k\big)\rangle_{(\mathbf{r})}\Big]$$

They are small because of the large nuclear masses M_A in the denominator.

In the first term one may write

$$\langle\phi_{k'}|\big(\boldsymbol{\nabla}_A\phi_k\big)\rangle_{(\mathbf{r})} = \frac{\langle\phi_{k'}|\Big[\boldsymbol{\nabla}_A, H_\mathsf{e}\Big]|\phi_k\rangle_{(\mathbf{r})}}{E_k(\mathbf{R}) - E_{k'}(\mathbf{R})}\,,$$

which shows that the coupling is small only when the electronic energies $E_k(\mathbf{R})$ and $E_{k'}(\mathbf{R})$ are well separated. This is normally the case, and the Born-Oppenheimer approximation holds.

For certain geometries $\mathbf{R}$ the energies $E_k(\mathbf{R})$ and $E_{k'}(\mathbf{R})$ may be equal: two (or more) electronic states are degenerate. The Born-Oppenheimer approximation breaks down.

Breakdown of the Born-Oppenheimer approximation

Examples:

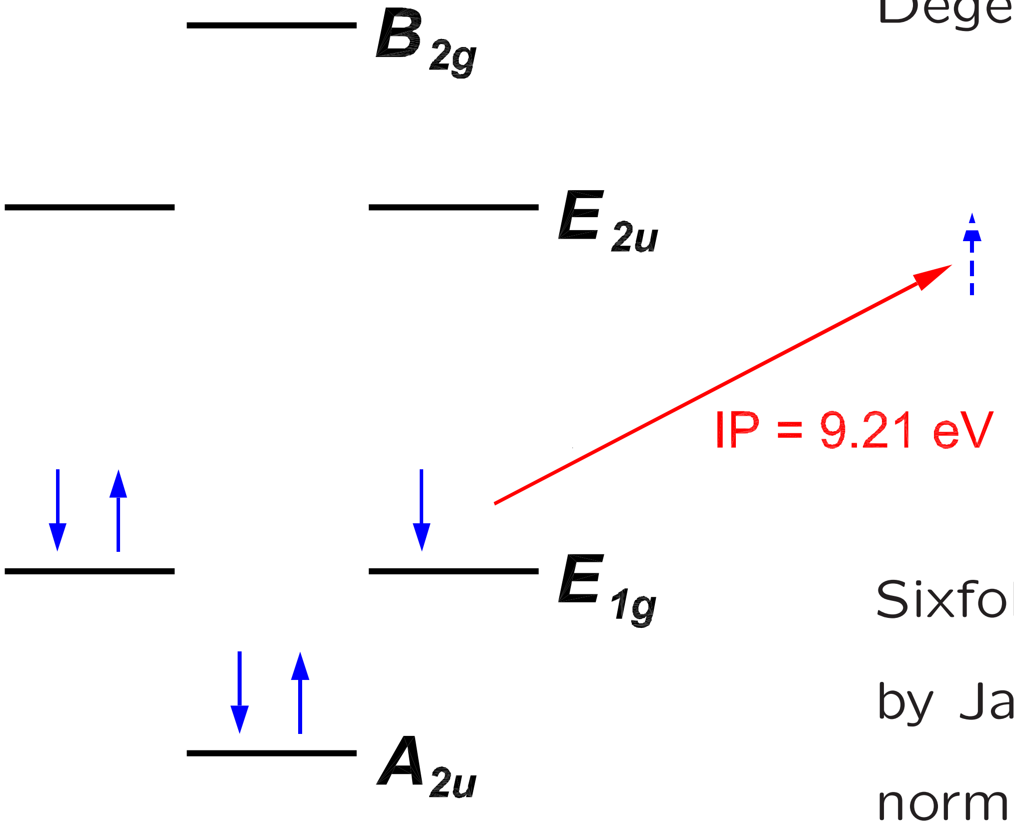
- Open-shell systems: radicals, molecules in excited states

  Degeneracies at symmetric structures
  $\Rightarrow$ Jahn-Teller, Renner-Teller distortions

  (Conical) intersections of different potential surfaces
  important in photochemistry

- Metals

Jahn-Teller effect in Benzene$^+$



π molecular orbitals

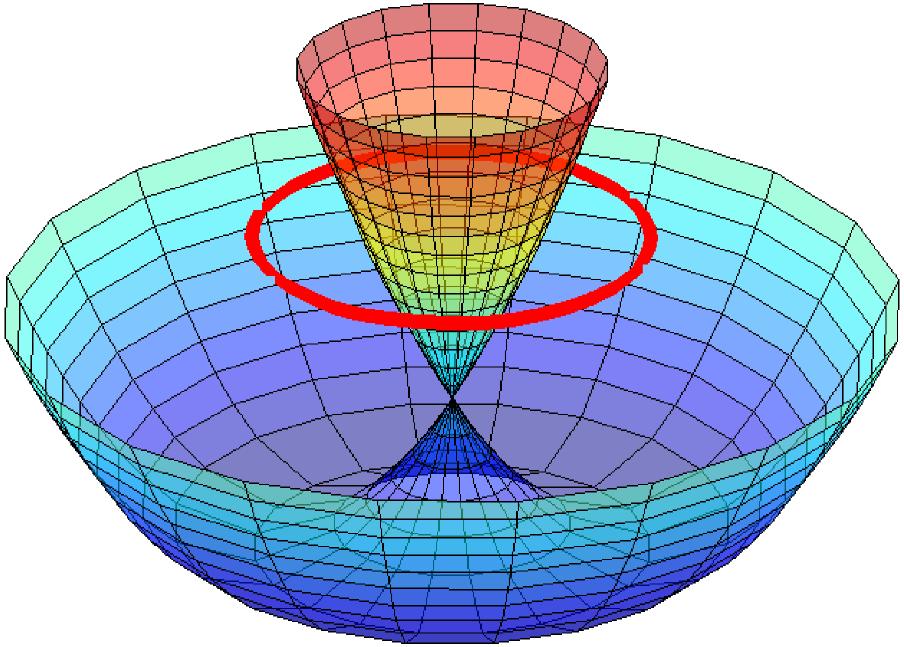
Degenerate ground state E_{1g}

Sixfold symmetry distorted

by Jahn-Teller coupling with

normal modes of e_{2g} symmetry

Potential surfaces



Two adiabatic potentials

corresponding to the E_{1g} state

as functions of the two ν_6

e_{2g} normal mode coordinates

Red circle shows the vibrational zero-point level

⇒ dynamic Jahn-Teller effect

Conical intersection

between

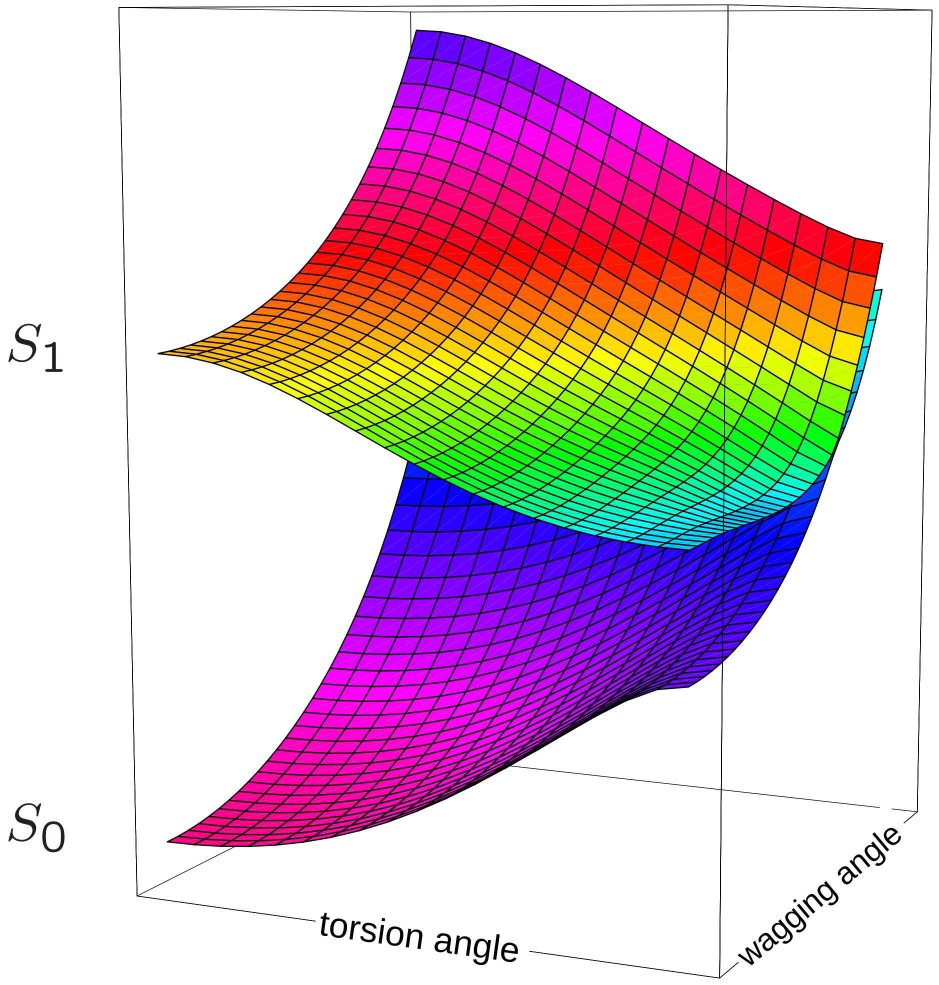
excited S_1 and

ground state S_0

potentials

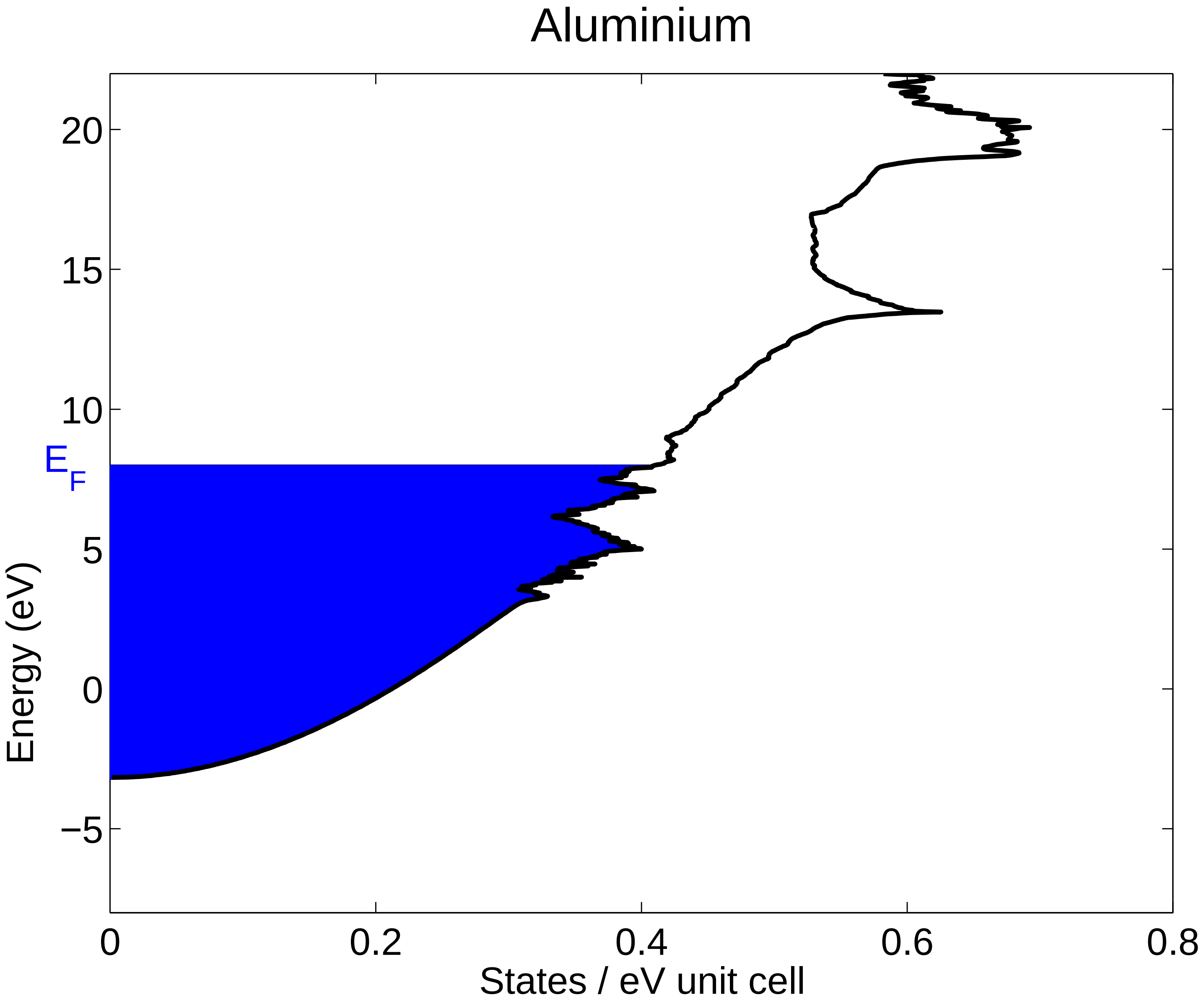
of ethene

C_2H_4

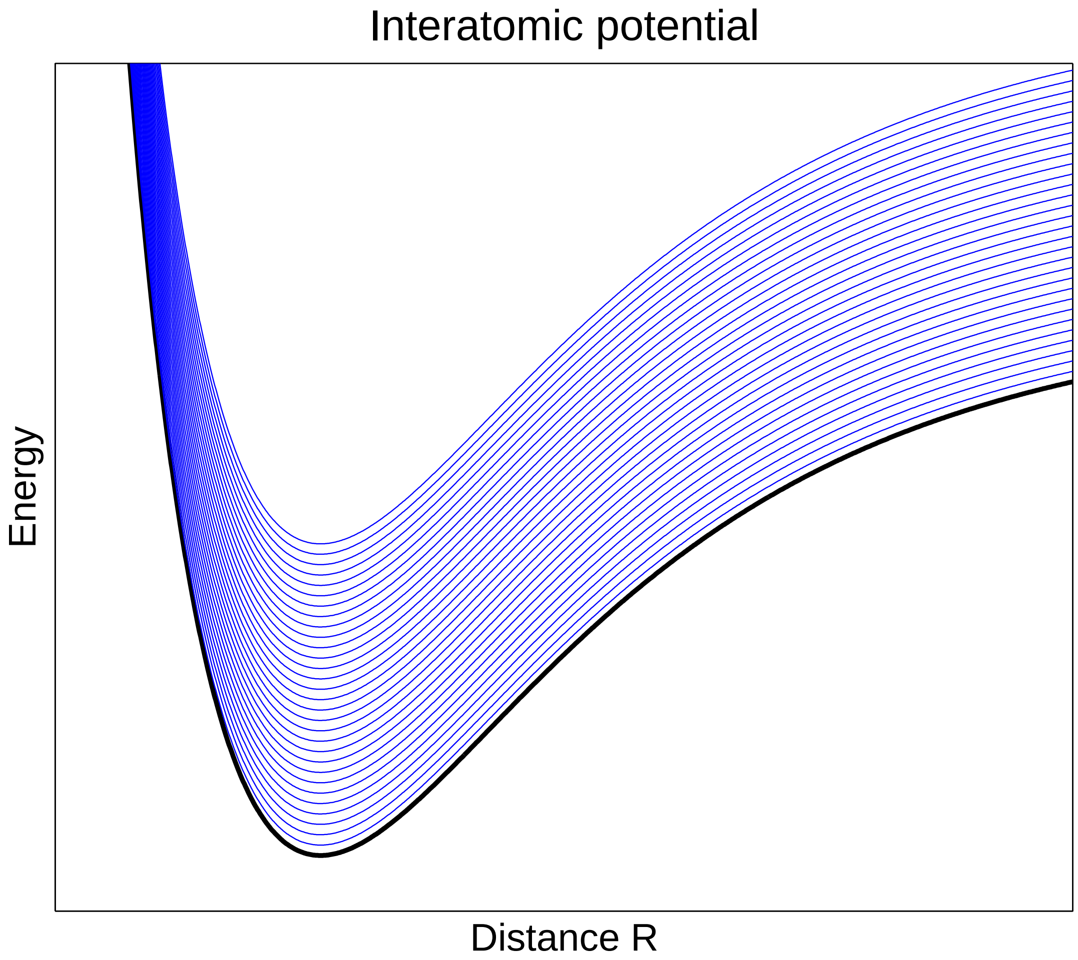


Fast non-radiative transition to ground state through non-adiabatic coupling prevents UV radiation damage in DNA

Metals


Aluminium
E_F
Energy (eV)
States / eV unit cell
20
15
10
5
0
−5
0
0.2
0.4
0.6
0.8

For metals



⇒ electron-phonon (non-adiabatic) coupling

How were intermolecular forces discovered?

Equation of state of a gas

Ideal gas

$$pV = kT$$

Non-ideal gas (Van der Waals, 1873)

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

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

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

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

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1927 / 1930

Wang, London: QM $\Rightarrow$ 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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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)

$$\begin{tikzcd}
0 \arrow[r, "\lambda"] & 1 \\
H^{(0)} \arrow[r, "H(\lambda)"] & H \\
E_k^{(0)} \arrow[r, "E_k(\lambda)"] & E_k \\
\Phi_k^{(0)} \arrow[r, "\Phi_k(\lambda)"] & \Phi_k
\end{tikzcd}$$

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

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

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

and perturbation

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

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

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

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

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

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

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

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

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

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

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

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

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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.

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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 $j \in B$.

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

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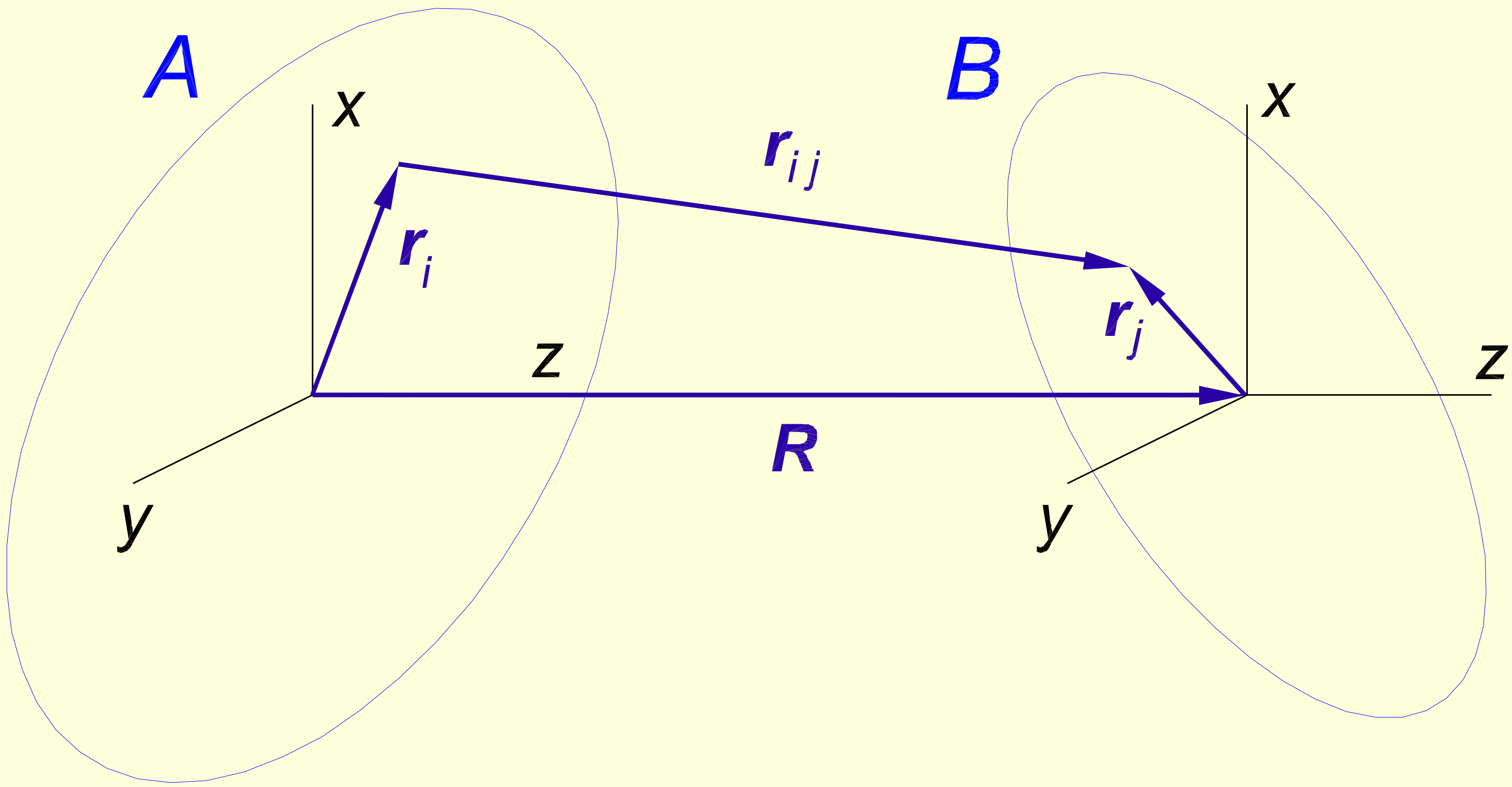
Same as $H^{(1)} = \sum_{i=1}^{n} q_i V(\boldsymbol{r}_i)$ in previous section with

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

of molecule B.

Multipole expansion of the interaction operator



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

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

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

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

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

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

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

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

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

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

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

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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

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

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

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

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

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

Proof

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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

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

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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

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

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

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

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

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

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

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

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

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.

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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

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

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

$$E_0^{(2)}(\mathrm{disp})$$

$$= \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \frac{\langle\, \Phi_0^A \Phi_0^B \mid H^{(1)} \mid \Phi_{k_1}^A \Phi_{k_2}^B \,\rangle \langle\, \Phi_{k_1}^A \Phi_{k_2}^B \mid H^{(1)} \mid \Phi_0^A \Phi_0^B \,\rangle}{(E_0^A - E_{k_1}^A) + (E_0^B - E_{k_2}^B)}$$

$$= -R^{-6} \sum_{k_1 \neq 0} \sum_{k_2 \neq 0} \frac{\left| \langle\, \Phi_0^A \mid \boldsymbol{\mu}^A \mid \Phi_{k_1}^A \,\rangle \cdot \boldsymbol{T} \cdot \langle\, \Phi_0^B \mid \boldsymbol{\mu}^B \mid \Phi_{k_2}^B \,\rangle \right|^2}{(E_{k_1}^A - E_0^A) + (E_{k_2}^B - E_0^B)}$$

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 $\langle \boldsymbol{\mu}^A \rangle, \langle \boldsymbol{\mu}^B \rangle$ 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.

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

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

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 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.

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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

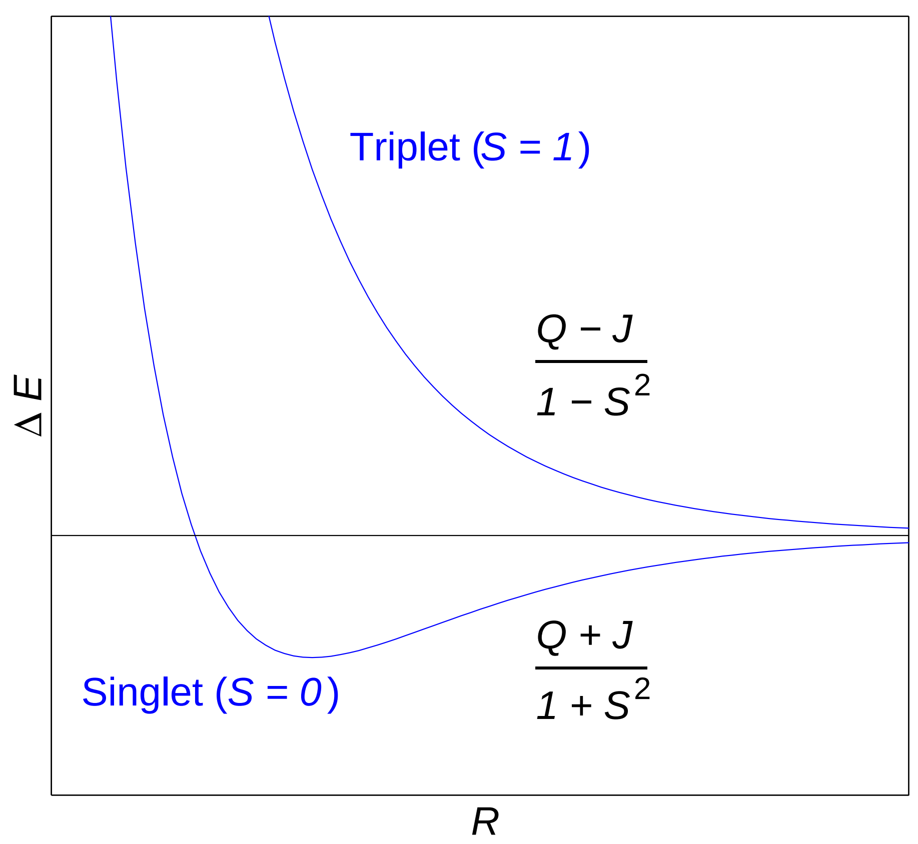
$$\alpha(1)\beta(2) - \beta(1)\alpha(2)$$

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”

$S(R) = \langle\, 1s_A \mid 1s_B \,\rangle$
= 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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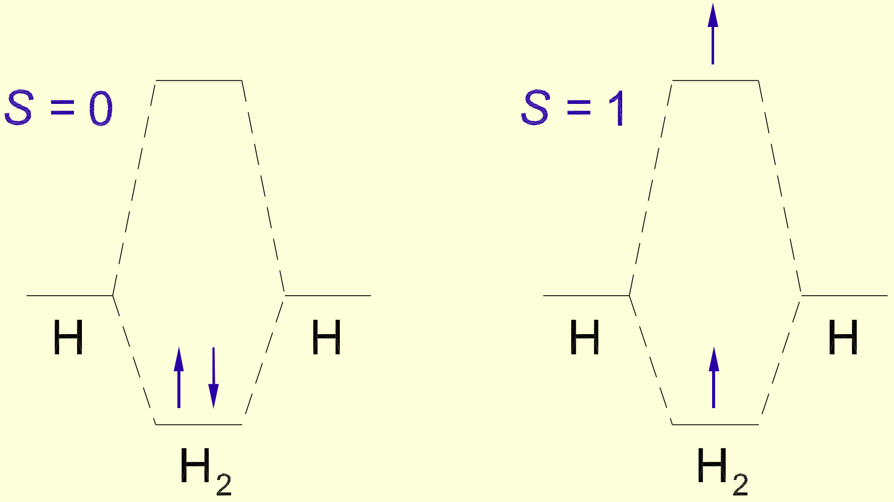
For He$_2$ there is only one (singlet) state and the interaction energy $\Delta E(R)$ is purely repulsive: exchange (or Pauli) repulsion or steric hindrance.

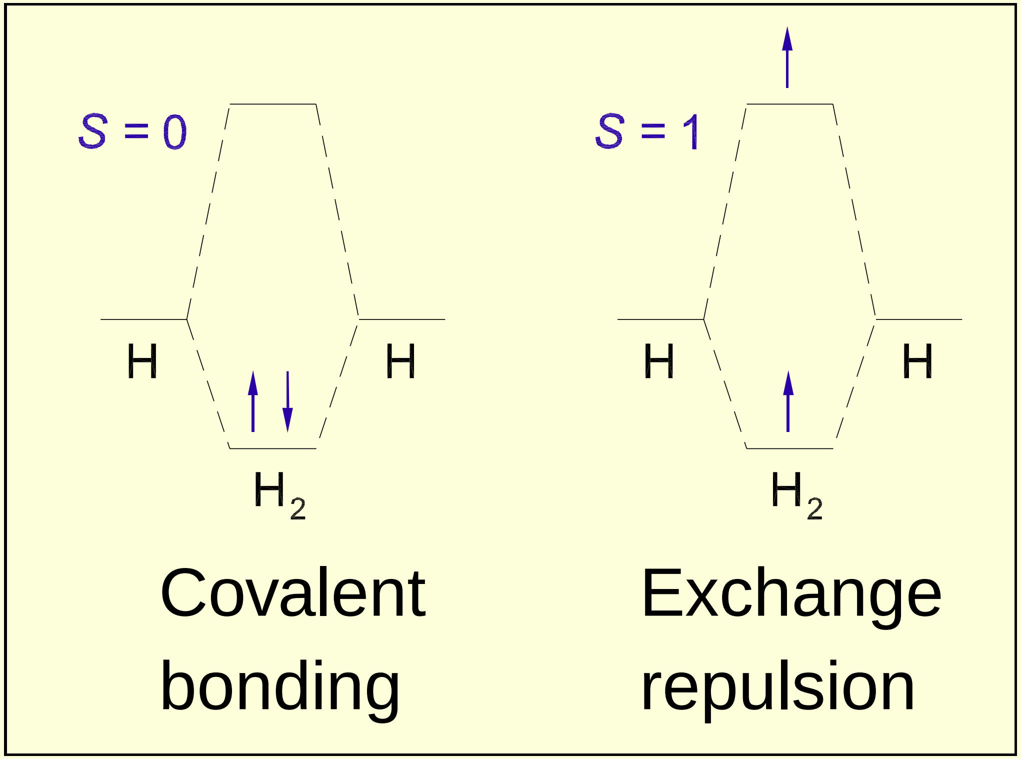
Molecular orbital picture



Covalent bonding

Exchange repulsion

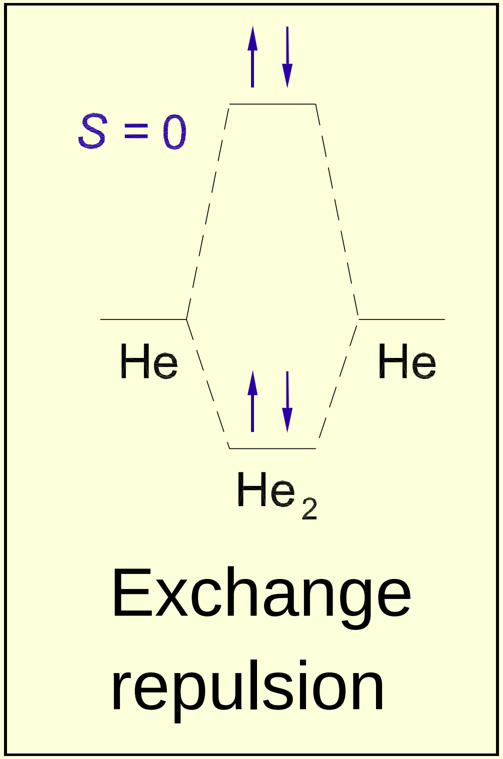
Molecular orbital picture



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.

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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. $\mathrm{Na}^{+}\mathrm{Cl}^{-}$).

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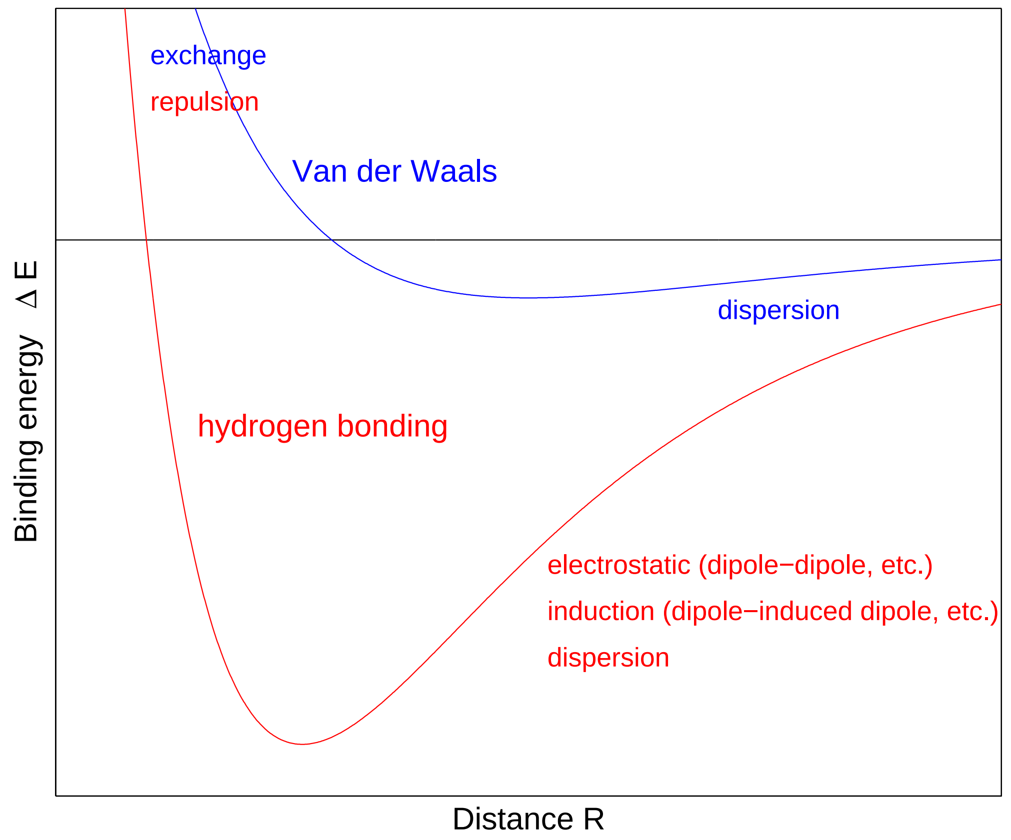
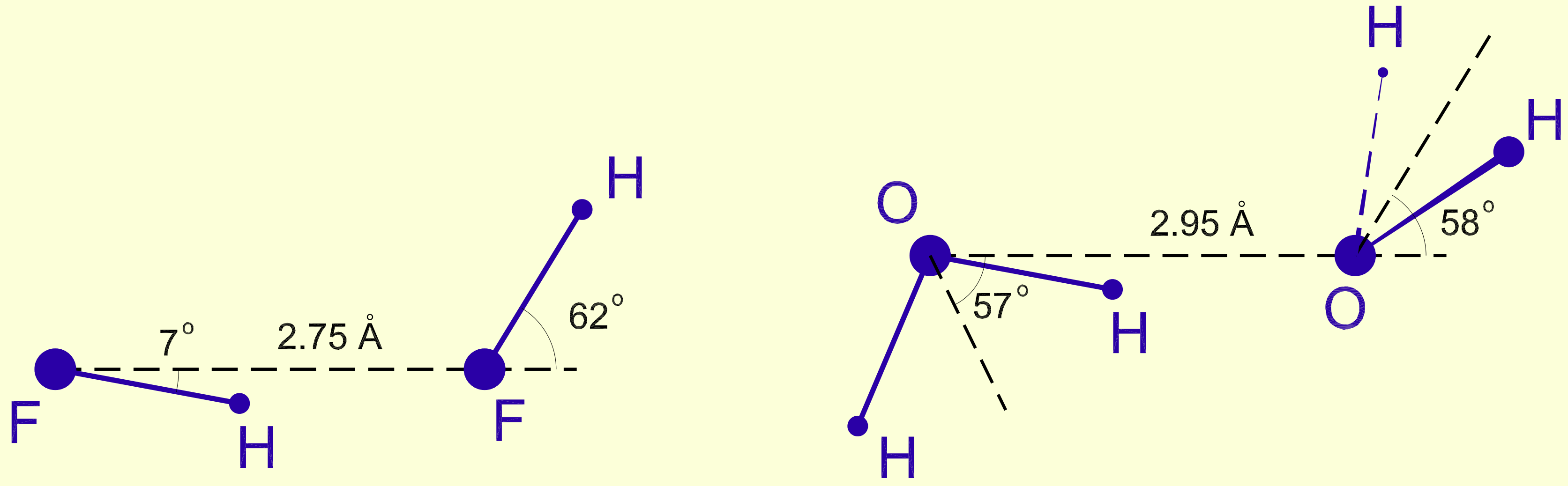
Binding (merely by the attractive dispersion energy) is weakest when both molecules are neutral and non-polar: pure Van der Waals interactions.

A special type of interactions between polar molecules is *hydrogen bonding:* X–H· · · Y



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

Exercise:



Compute the equilibrium angles of HF–HF at $R = 2.75$ 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).

Non-covalent force fields computed *ab initio*

- 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.

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 $\Phi^{A}_{k_1}$ 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 $\Rightarrow$ Many-body SAPT.

Program packages:

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

Most difficult: dispersion interactions

First *ab initio* calculation of He–He binding curve:

Phys. Rev. Letters, **25** (1970)

- H.F. Schaefer, D.R. McLaughlin, F.E. Harris, and B.J. Alder
  page 988: $D_e = 12.0$ K
- P. Bertoncini and A. C. Wahl
  page 991: $D_e = 11.4$ K

Present value:

$D_e = 11.01$ K $= 7.65$ cm^{-1}

≈ 0.1 kJ/mol $\approx 10^{-3}$ eV $\approx 3.5 \times 10^{-5}$ Hartree

Can one use DFT methods?

Reviews by Johnson & DiLabio, Zhao & Truhlar

Many different functionals tested with different basis sets

type	dimer	mean error in D_e
Van der Waals	Rg_2, $(CH_4)_2$, $(C_2H_2)_2$, $(\text{benzene})_2$	40 - 200 %
dipole-induced dipole	CH_4–HF, H_2O–benzene, etc.	15 - 100 %
dipole-dipole	$(H_2CO)_2$, etc.	10 - 40 %
hydrogen bonded	$(NH_3)_2$, $(H_2O)_2$, $(HCOOH)_2$, etc.	3 - 20%

- Some VdW dimers, $(\text{benzene})_2$ for example, not bound
- B971 best, B3LYP worst
- Often best results without BSSE correction, or smaller basis sets
  ⇒ Right for wrong reason

Basic problems with DFT

1. Exchange repulsion

– Incorrect asymptotic behavior of one-electron potential:
$v(r) \to \exp(-\alpha r)$ instead of $-1/r$

– In intermolecular Coulomb energy no self-term present
self-exchange $\Rightarrow$ spurious attraction

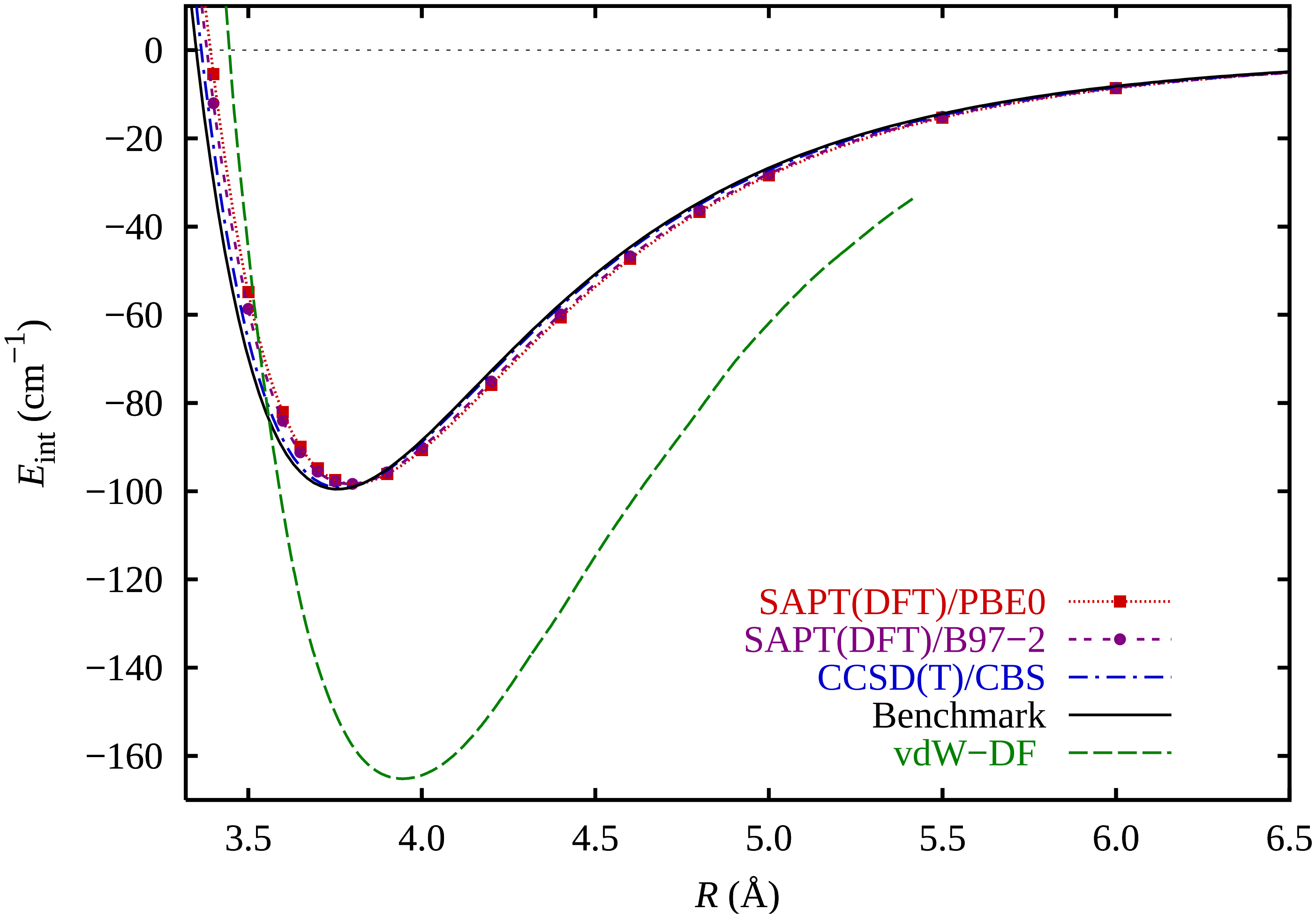
2. Dispersion

– Intrinsically non-local:
cannot be described by local LDA or semi-local GGA methods

DFT with dispersion explicitly included

vdW-DF: M. Dion, H. Rydberg, E. Schroder, D.C. Langreth, B.I. Lundqvist, Phys. Rev. Lett. **92** (2004) 246401

Ar–Ar interaction



From: R. Podeszwa and K. Szalewicz, Chem. Phys. Lett. **412** (2005) 488

DFT+D methods

- Compute interaction energy with “standard” DFT

- Add atom-atom $C_n r^{-n}$ long range dispersion terms with $n = 6, \ldots$

- Switch between short range correlation contained in DFT and the long range terms with a smooth (parameterized) switch function

- Parameters from atomic electron densities, polarizabilities, etc. (Becke & Johnson, Tkatchenko & Scheffler)

- Empirically optimized parameters (Yang, Grimme)

Alternative: SAPT-DFT

Implemented by G. Jansen *et al.* (Essen) and K. Szalewicz *et al.* (Delaware)

- First order SAPT energy (electrostatic + exchange) computed with monomer densities and density matrices from Kohn-Sham DFT
- Second-order SAPT energy (induction, dispersion + exchange) from (time-dependent) coupled perturbed Kohn-Sham response functions

Only Hartree-Fock like expressions from Many-Body SAPT needed $\Rightarrow$ better scaling

Caution !

- SAPT-DFT requires XC potential that is good in inner region and has correct $-1/r$ behavior for $r \to \infty$

- Coupled time-dependent DFT must be used for (frequency-dependent) density-density polarizabilities $\alpha(\boldsymbol{r}, \boldsymbol{r}', \omega)$

Both groups, K. Szalewicz (Delaware) and G. Jansen (Essen), further improved efficiency by implementation of density fitting.

Ar–Ar interaction

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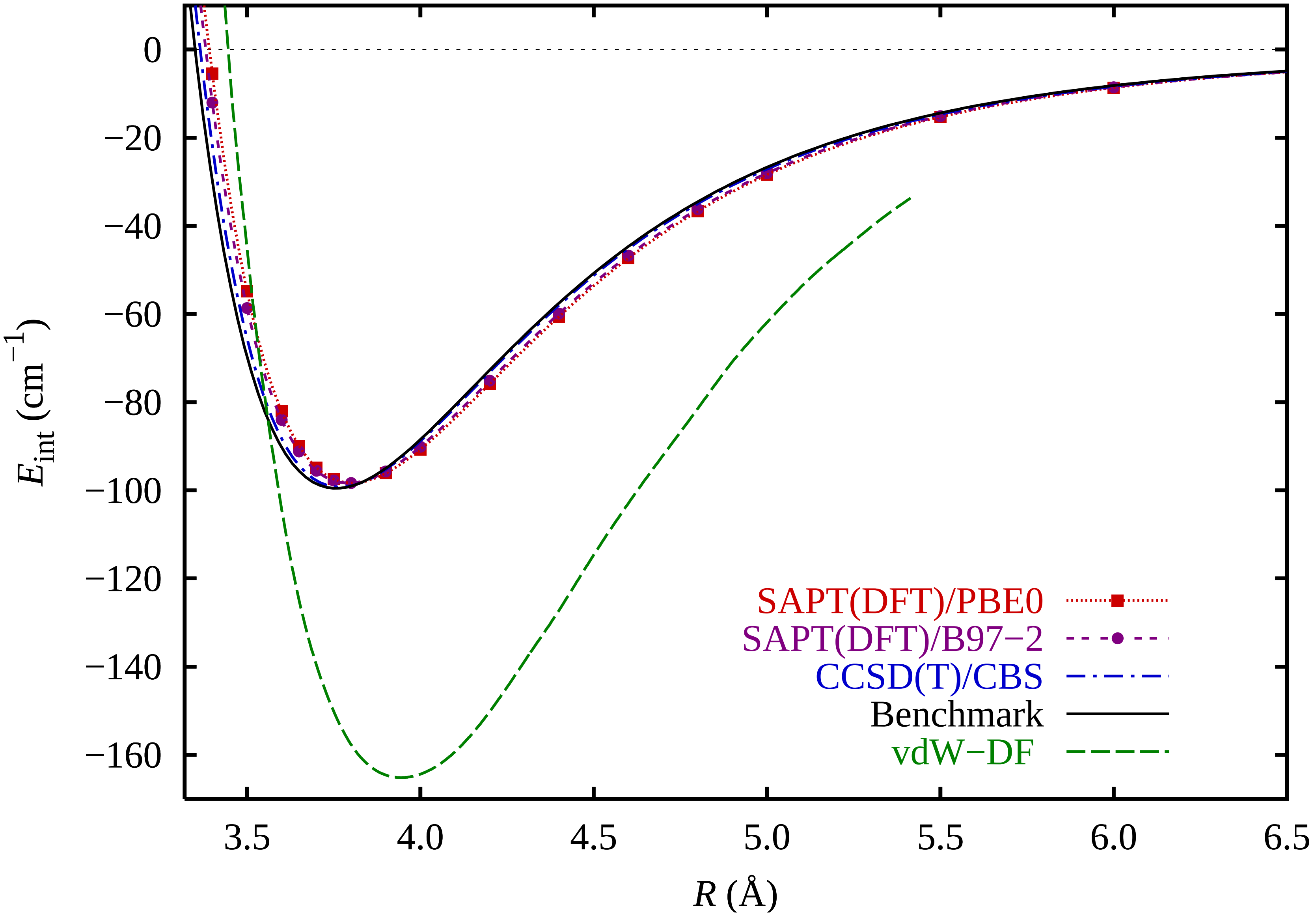
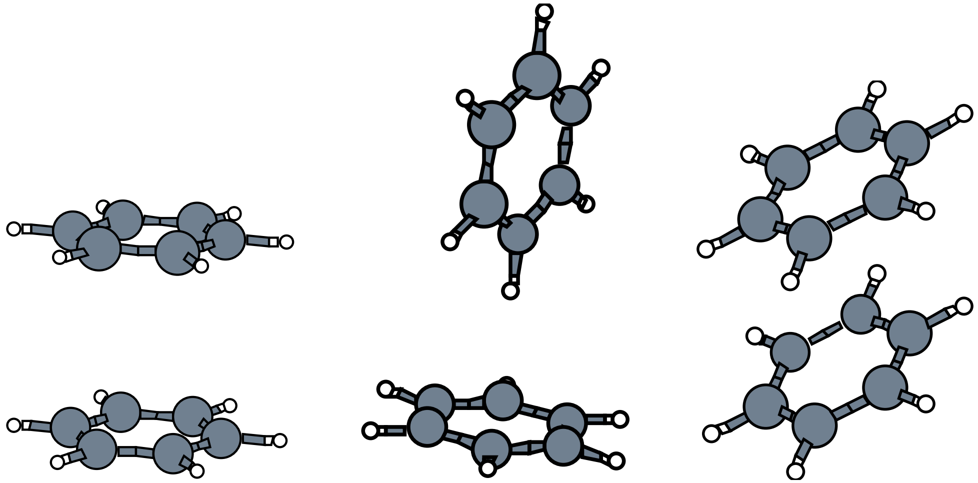


A. Heßelmann, G. Jansen, M. Schütz, J. Chem. Phys. **122** (2005) 014103

(benzene)$_2$

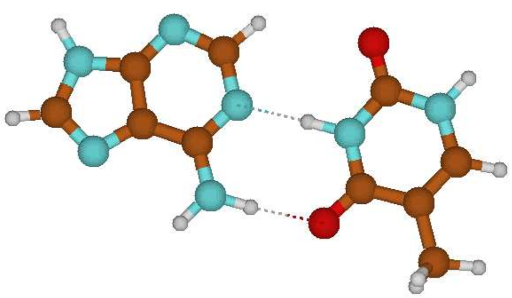
1512 GTOs (aug-cc-pVQZ), extrapolation to basis set limit

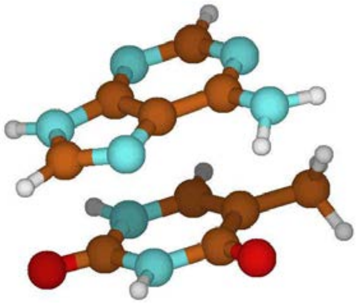


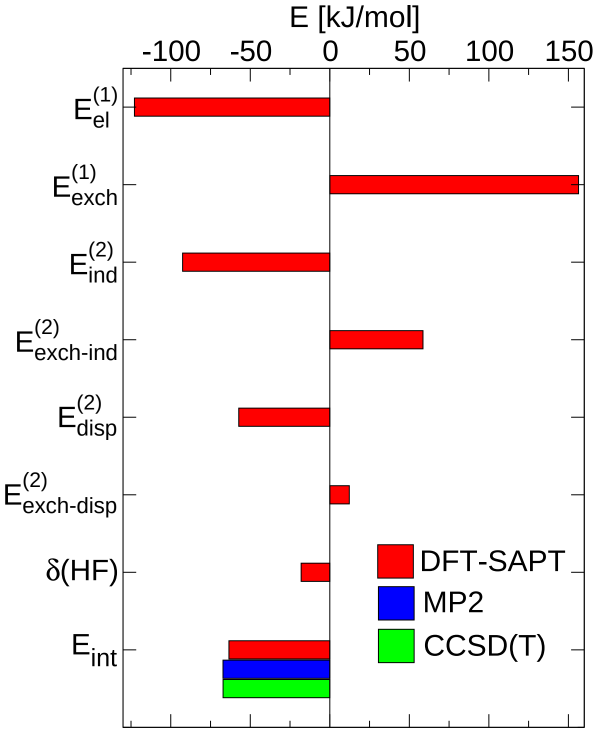
MP2	−14.4	−15.1	−20.3	kJ/mol
CCSD(T)	−6.7	−11.8	−11.4	
DF-SAPT-DFT	−7.6	−11.9	−12.7	
standard DFT	unbound	metastable	unbound	

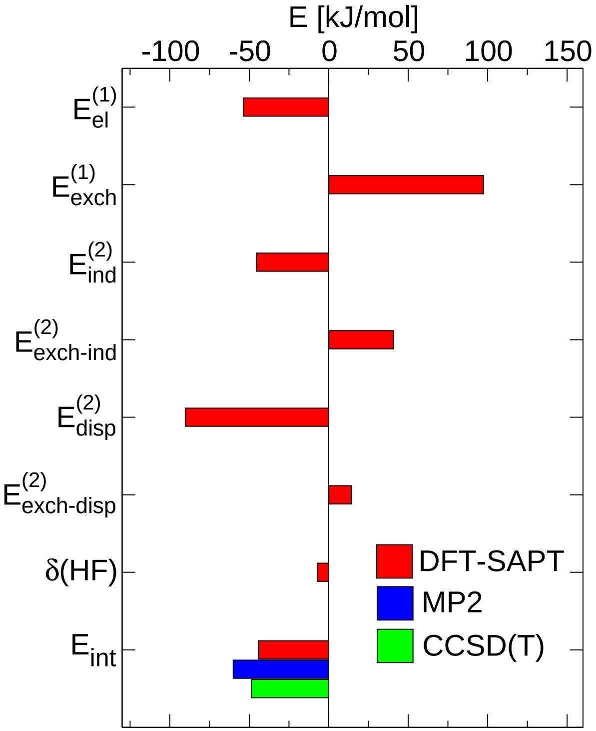
Adenine-Thymine (G. Jansen *et al.*)

DF-SAPT-DFT up to aug-cc-pVQZ level

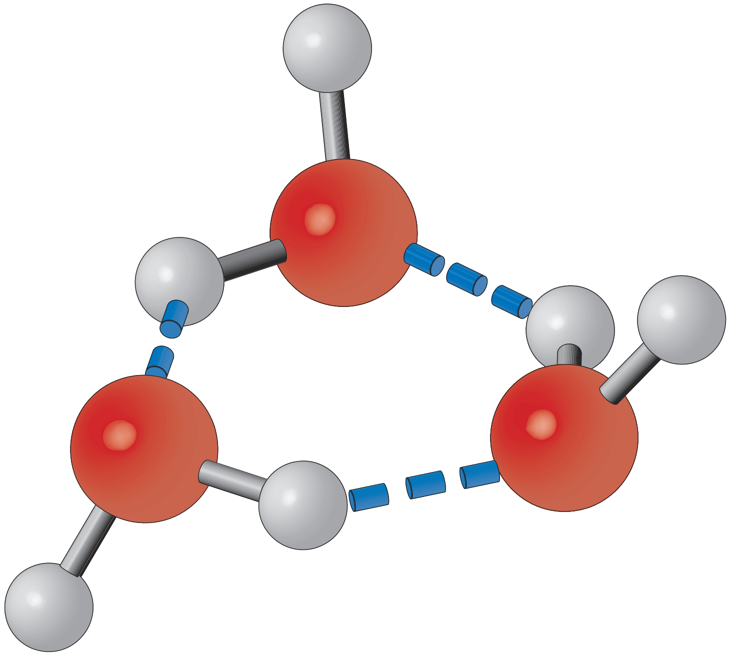


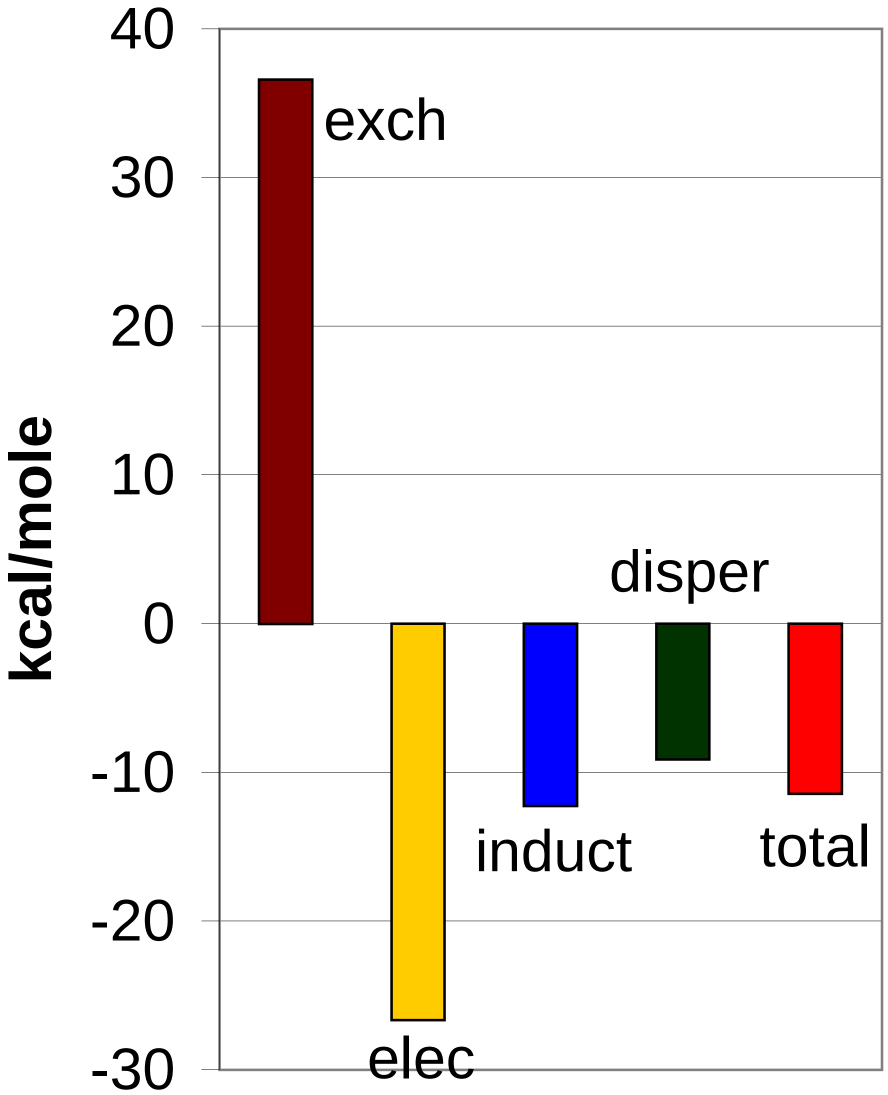




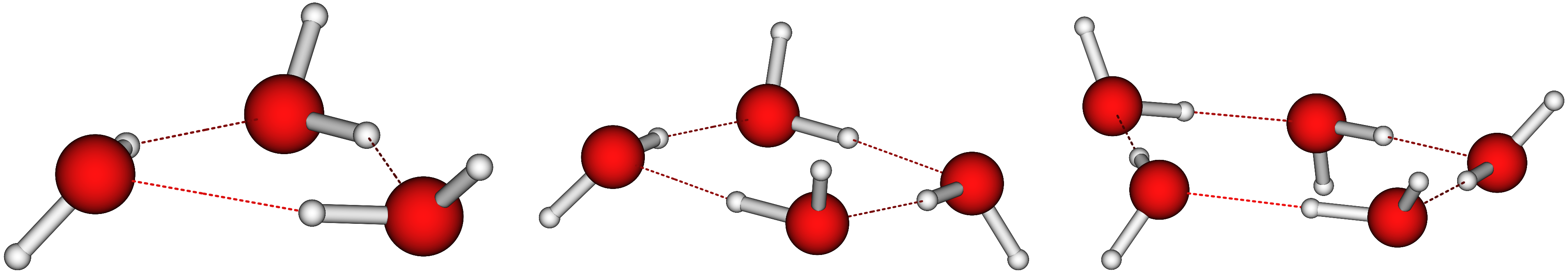


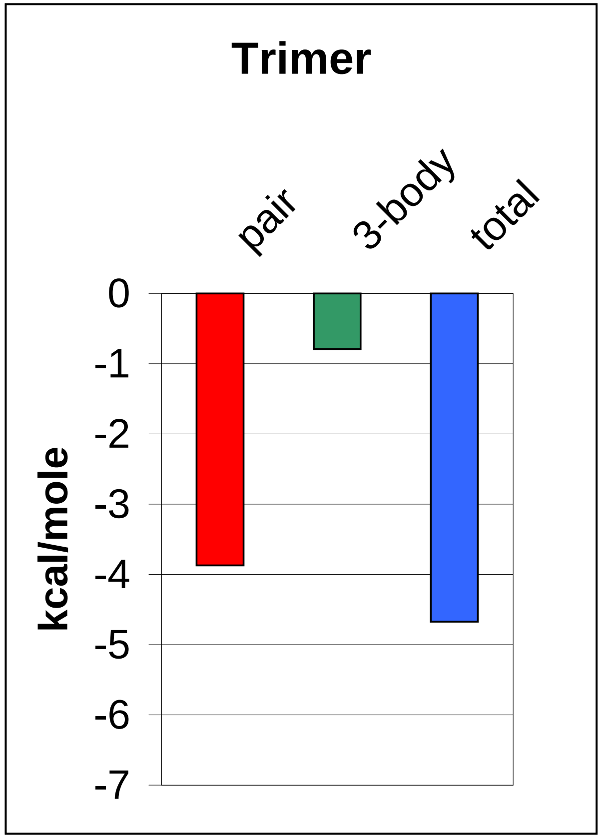
Pair interactions in water trimer



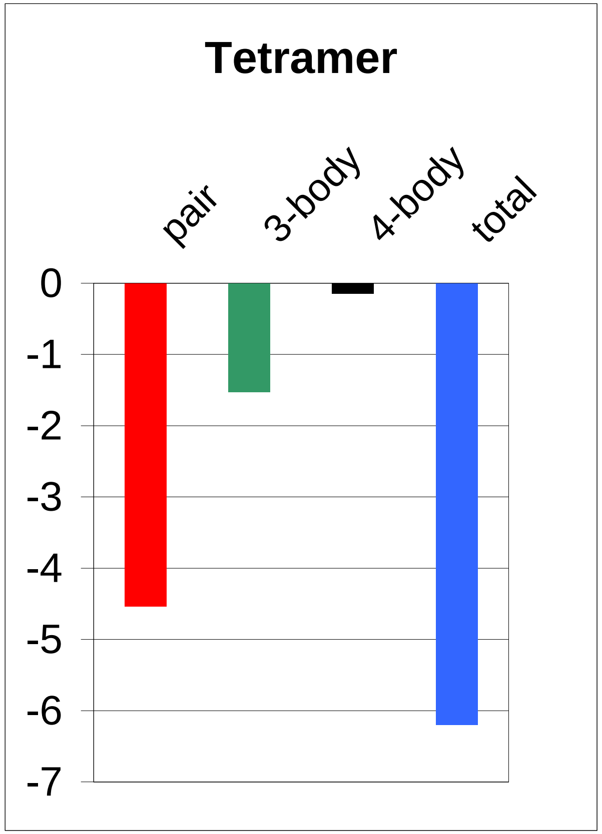


Many-body interactions (per hydrogen bond)

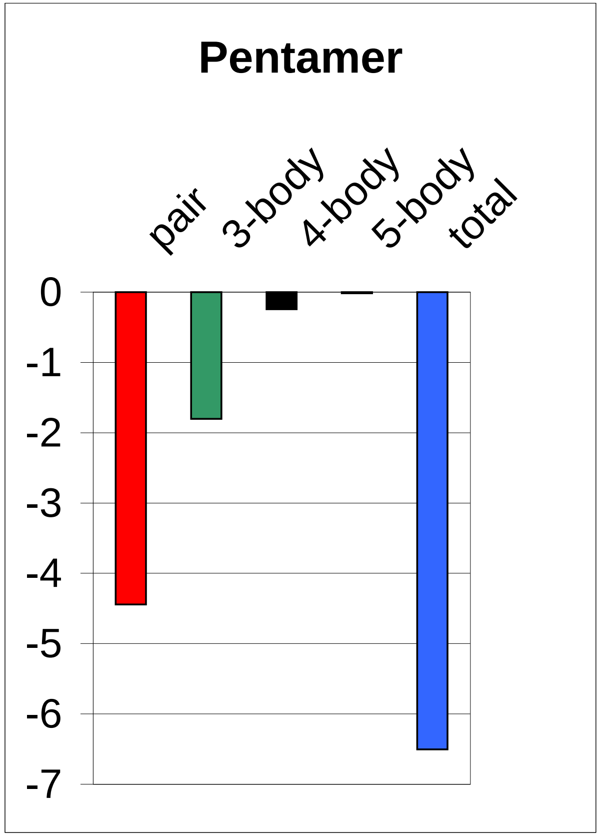




Trimer



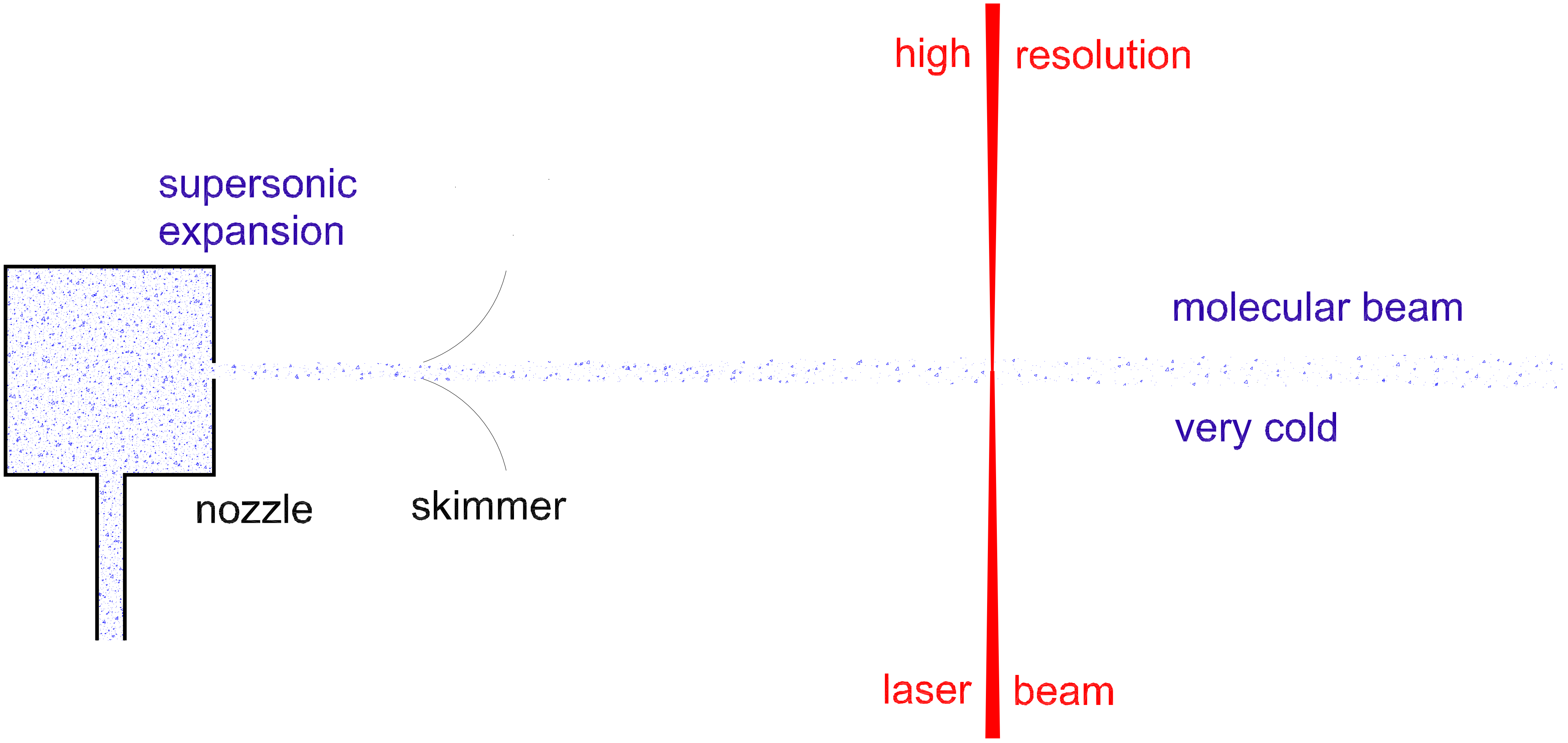
Tetramer



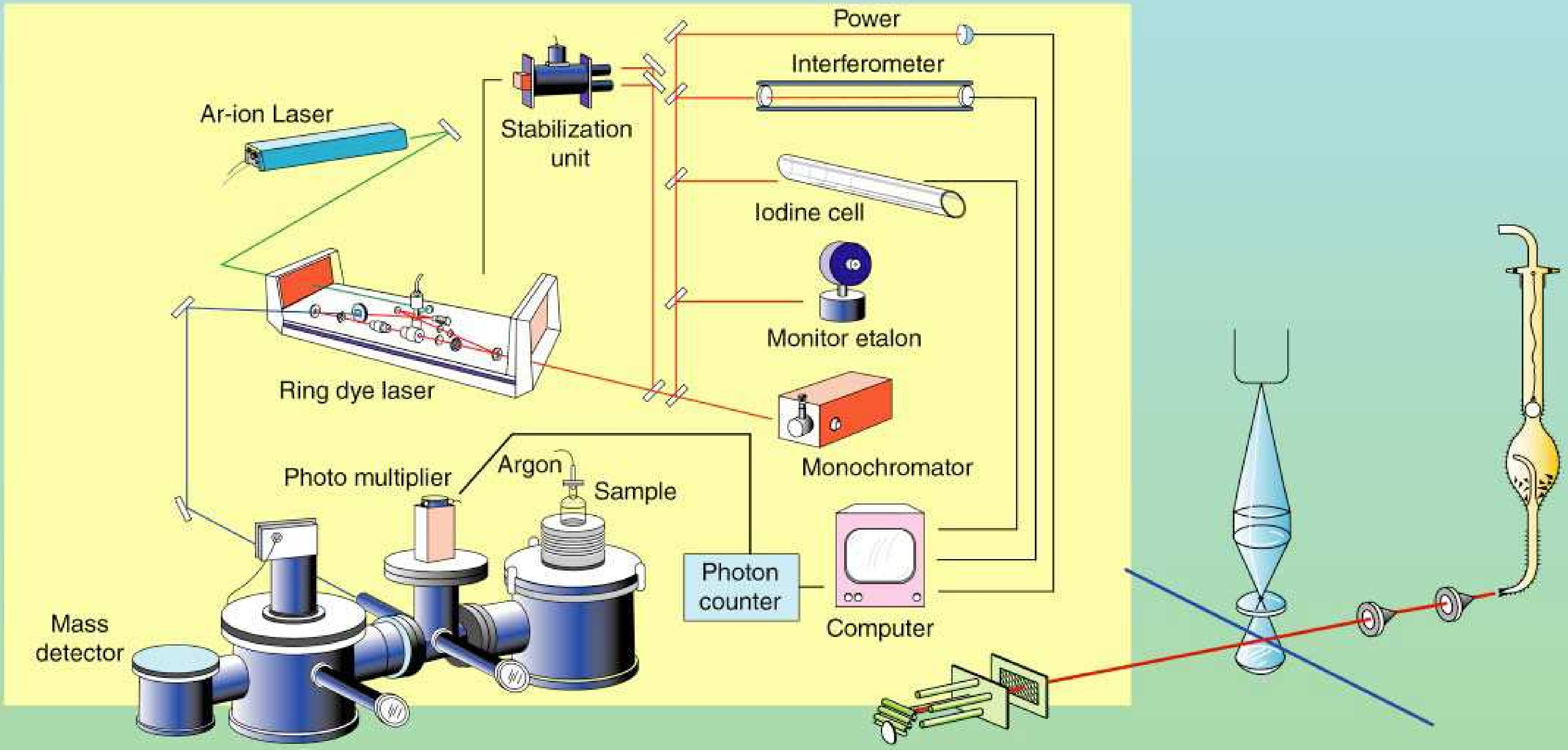
Pentamer

How to test non-covalent force fields?

Molecular beam spectroscopy of Van der Waals molecules



Experimental Set-Up



Intermolecular potential

⇓

Cluster (Van der Waals molecule)
quantum levels,
i.e.,
eigenstates of
nuclear motion Hamiltonian

⇓

Van der Waals spectra

Nuclear motion Hamiltonian $H = T + V$ for "normal" (= semi-rigid) molecules

- single equilibrium structure
- small amplitude vibrations

Use rigid rotor/harmonic oscillator model

For (harmonic) vibrations

- Wilson $\boldsymbol{GF}$-matrix method ⇒ frequencies, normal coordinates

Rigid rotor model ⇒ fine structure (high resolution spectra)

Nuclear motion Hamiltonian $H = T + V$ for weakly bound complexes (Van der Waals or hydrogen bonded)

- multiple equivalent equilibrium structures
  (= global minima in the potential surface V)

- small barriers ⇒ tunneling between minima

- large amplitude (VRT) motions:
  vibrations, internal rotations, tunneling
  (more or less rigid monomers)

- curvilinear coordinates
  ⇒ complicated kinetic energy operator T

Method for molecule-molecule dimers

H_2O–H_2O, NH_3–NH_3, C_6H_6–C_6H_6, etc.

Hamiltonian

$$H = T_A + T_B - \frac{\hbar^2}{2\mu R}\frac{\partial^2}{\partial R^2}R + \frac{(\boldsymbol{J} - \boldsymbol{j}_A - \boldsymbol{j}_B)^2}{2\mu R^2} + V(R, \boldsymbol{\omega}_A, \boldsymbol{\omega}_B)$$

Monomer Hamiltonians ($X = A, B$):

$$T_X = A_X\,(j_X)_a^2 + B_X\,(j_X)_b^2 + C_X\,(j_X)_c^2$$

Basis for bound level calculations

$$\chi_n(R)\; D^{(J)}_{MK}(\alpha,\beta,0)^* \sum_{m_A,m_B} D^{(j_A)}_{m_A k_A}(\boldsymbol{\omega}_A)^* D^{(j_B)}_{m_B k_B}(\boldsymbol{\omega}_B)^* \langle\, j_A, m_A; j_B, m_B \mid j_{AB}, K\,\rangle$$

Wave function expansion

$$\Psi_k(R,\boldsymbol{\omega}_A,\boldsymbol{\omega}_B,\Theta,\Phi)=\sum_i |\, i\,\rangle\, c_{ik}$$

yields matrix eigenvalue problem

$$\boldsymbol{H}\boldsymbol{c}_k = E_k\boldsymbol{c}_k \quad \text{with} \quad H_{ij}=\langle\, i \,|\, H \,|\, j\,\rangle$$

dimension $\leq 300\,000$ for water dimer

Lanczos/Davidson iterative methods

$\Rightarrow$ lowest 20 eigenvalues E_k and eigenvectors $\boldsymbol{c}_k$

Start with trial vectors $\boldsymbol{x}_k^{(0)}$

Calculate $\boldsymbol{H}\boldsymbol{x}_k^{(0)} \Rightarrow \boldsymbol{x}_k^{(1)}$

$\vdots$

Calculate $\boldsymbol{H}\boldsymbol{x}_k^{(n-1)} \Rightarrow \boldsymbol{x}_k^{(n)}$

$\vdots$

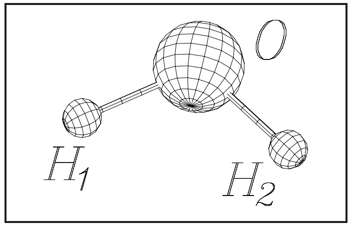
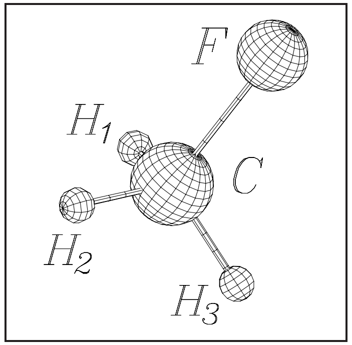
Iterate until $\boldsymbol{x}_k^{(n)}$ converged $\Rightarrow \boldsymbol{c}_k, E_k$

The permutation-inversion (PI) symmetry group

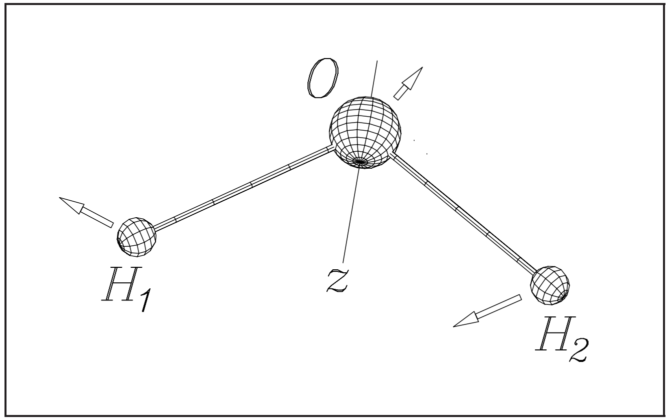
For semi-rigid molecules

Use *Point Group of Equilibrium Geometry* to describe the (normal coordinate) vibrations

N.B. This point group is isomorphic to the PI group, which contains all "feasible" permutations of identical nuclei, combined with inversion E^*.

Molecule	Point group	PI group
	C_{2v}	$\{E, E^*, (12), (12)^*\}$
	C_{3v}	$\{E, (123), (132),$ $(12)^*, (13)^*, (23)^*\}$

Example: H_2O



PI operation	frame rotation	point group operation
(12)	$R_z(\pi) = C_{2z}$	C_{2z}
E^*	$R_y(\pi) = C_{2y}$	σ_{xz} reflection
$(12)^*$	$R_x(\pi) = C_{2x}$	σ_{yz} reflection

permutation ⇒ frame rotation + point group rotation

permutation-inversion ⇒ frame rotation + reflection

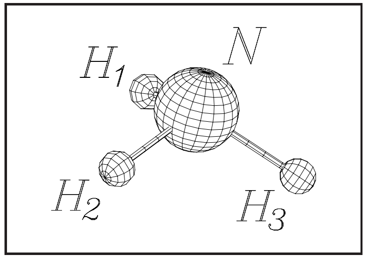
Hence: PI-group $\simeq$ point group

For “floppy” molecules/complexes

- multiple equivalent minima in V
- low barriers: tunneling between these minima is “feasible”.

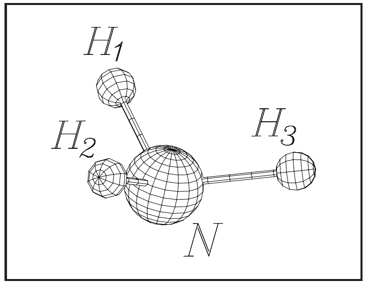
$\Rightarrow$ additional “feasible” PI-operations

Example NH_3



semi-rigid NH_3

$PI(C_{3v}) = \{E, (123), (132), (12)^*, (13)^*, (23)^*\}$



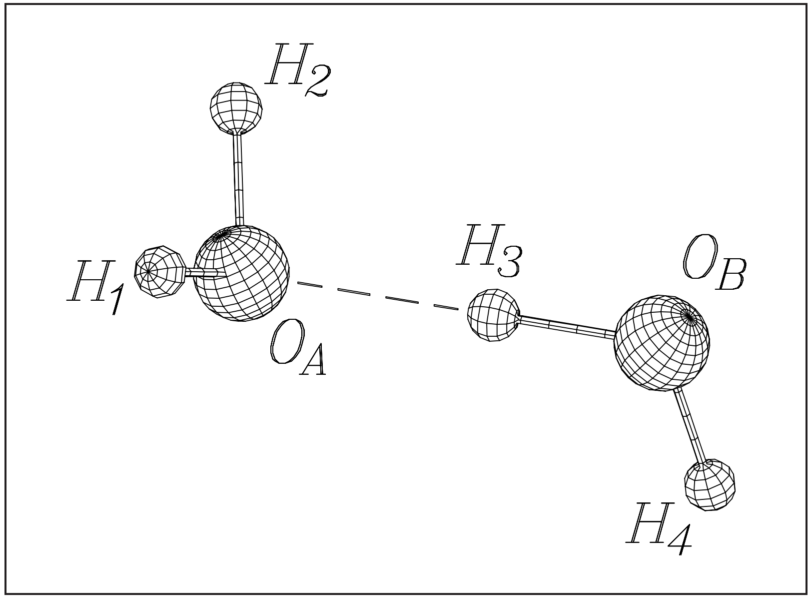
+ inversion tunneling (umbrella up ↔ down)

$PI(D_{3h}) = PI(C_{3v}) \otimes \{E, E^*\}$

Also $(12), (13), (23)$ and E^* are feasible

Additional feasible PI-operations $\iff$ observable tunneling splittings in spectrum

For H_2O–H_2O



PI group $G_{16} = \{E, P_{12}\} \otimes \{E, P_{34}\} \otimes \{E, P_{AB}\} \otimes \{E, E^*\}$

Equilibrium geometry has C_s symmetry

$\Rightarrow$ 8-fold tunneling splitting of rovib levels

Illustration:

Ab initio water potential

- Tested by spectroscopy on dimer and trimer
- Used in MD simulations for liquid water

R. Bukowski, K. Szalewicz, G.C. Groenenboom, and A. van der Avoird, Science, **315**, 1249 (2007)

Polarizable water pair potential: CC-pol

- From CCSD(T) calculations in aug-cc-pVTZ + bond function basis
- Extrapolated to complete basis set (CBS) limit at MP2 level
- 2510 carefully selected water dimer geometries
- Estimated uncertainty < 0.07 kcal/mol
  (same as best single-point calculations published)

CC-pol: Analytic representation

- Site-site model with 8 sites (5 symmetry distinct) per molecule
  - Coulomb interaction,
  - dispersion interaction,
  - exponential ‘overlap’ terms: first-order exchange repulsion, second-order exchange induction + dispersion

- Extra polarizability site for induction interaction

- Long range R^{-n} contributions computed by perturbation theory, subtracted before fit of short range terms

- Good compromise between accuracy of reproducing computed points (rmsd of 0.09 kcal/mol for $\Delta E < 0$) and simplicity needed for molecular simulations

Water cluster spectra (far-infrared, high-resolution)

from Saykally group (UC Berkeley)

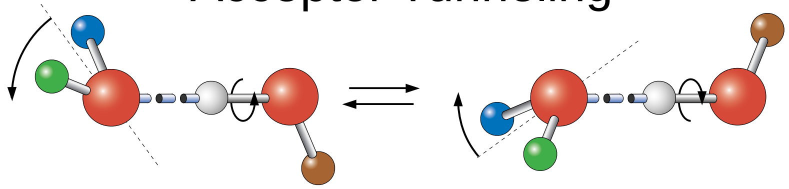
Used for test of potential:

Pair potential ⇒ Dimer VRT levels ⇒ Dimer spectrum

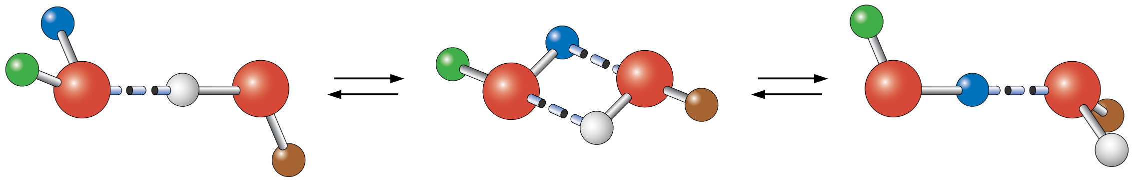
Pair + 3-body potential ⇒ Trimer VRT levels ⇒ Trimer spectrum

Water dimer tunneling pathways

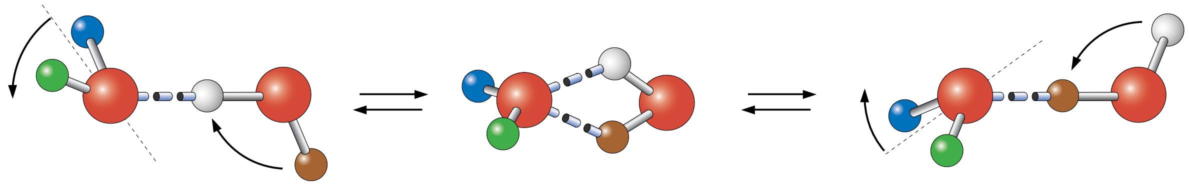
Acceptor Tunneling



Donor-Acceptor Interchange Tunneling

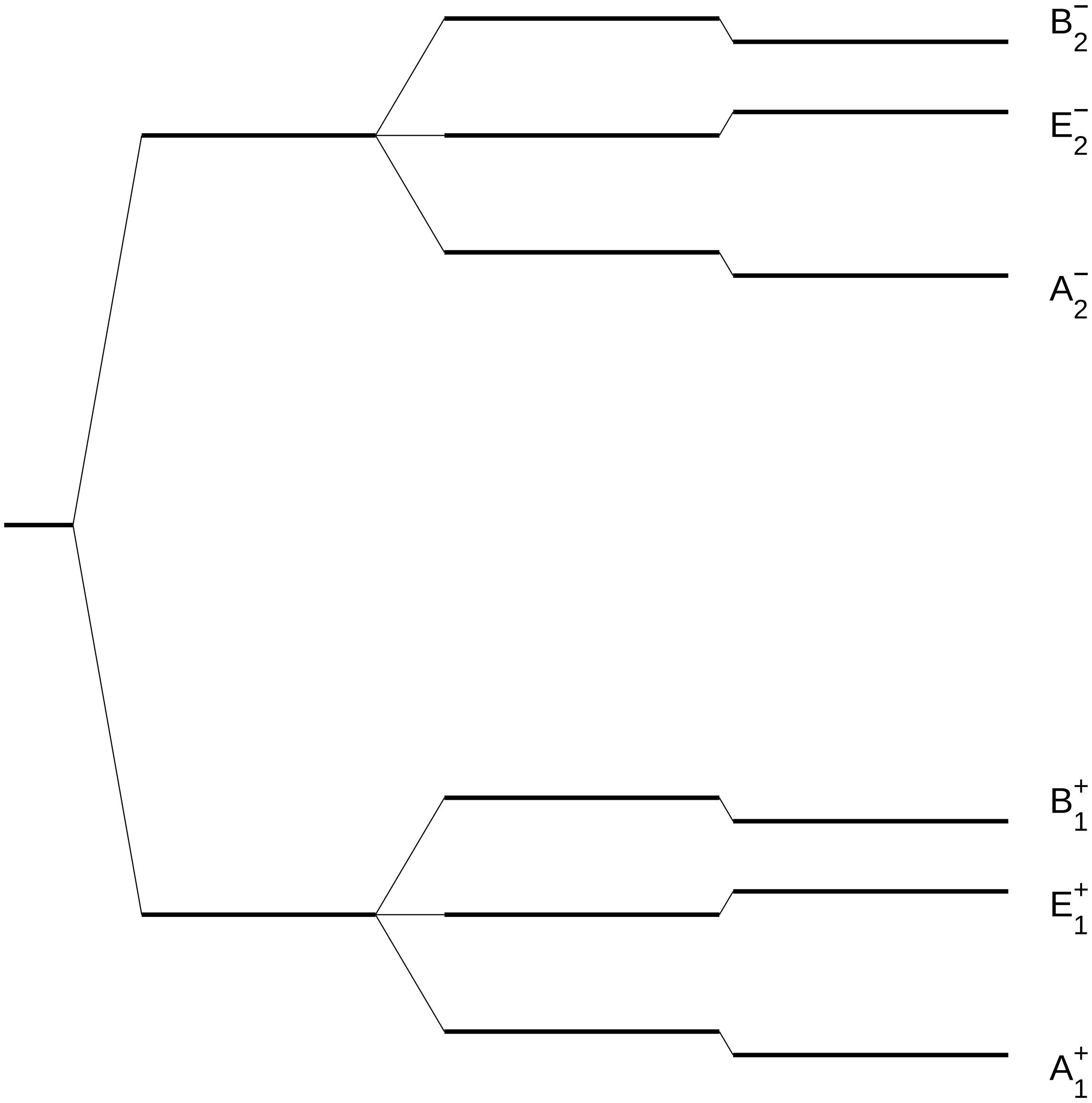


Donor (Bifurcation) Tunneling



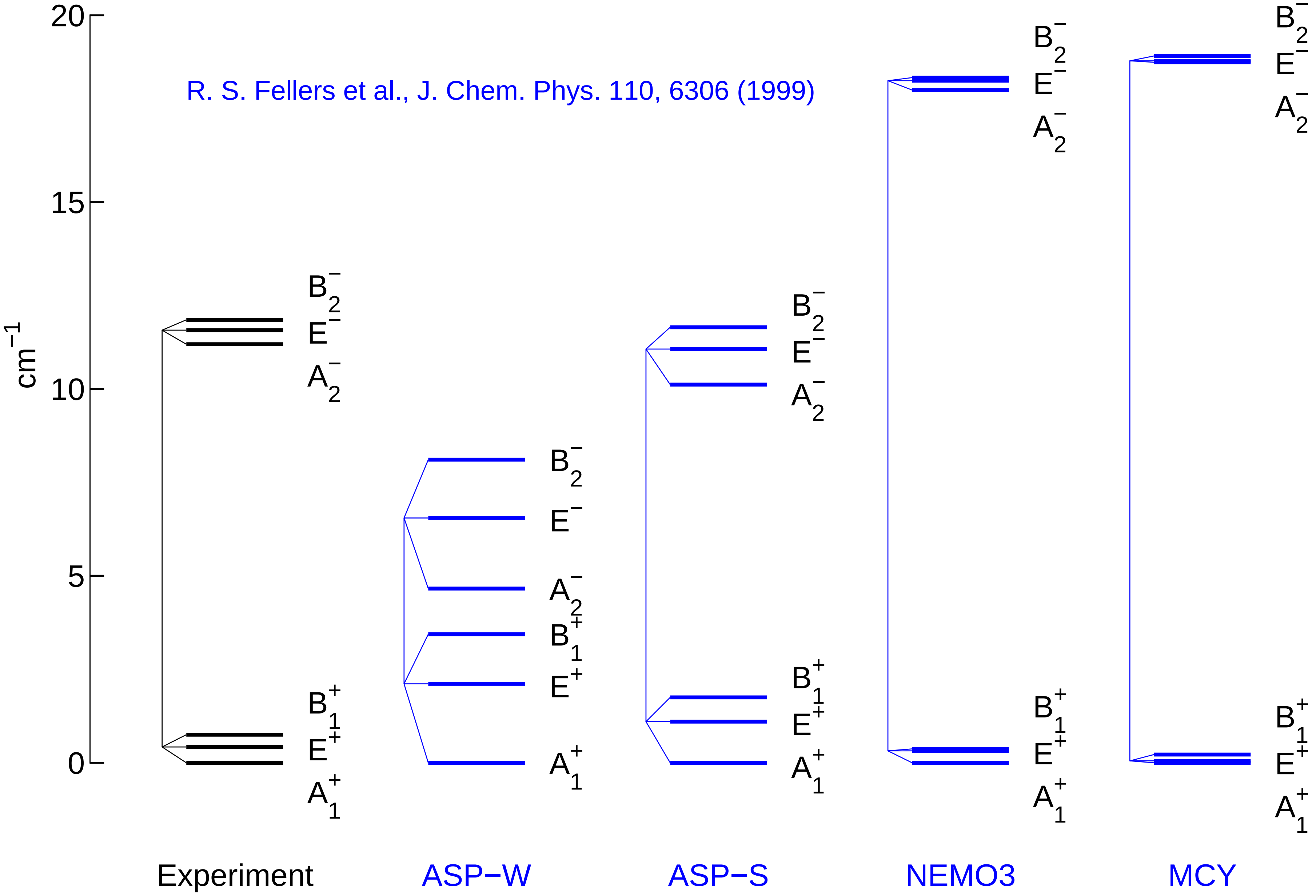
Water dimer tunneling levels

$(J = K = 0)$



Acceptor tunneling → Interchange tunneling → Bifurcation tunneling

$(H_2O)_2$ levels computed from various potentials (J=K=0)



R. S. Fellers et al., J. Chem. Phys. 110, 6306 (1999)

H_2O dimer

tunneling levels

from CC-pol-8s

potential (2008

Szalewicz *et al.*)

and

experiment

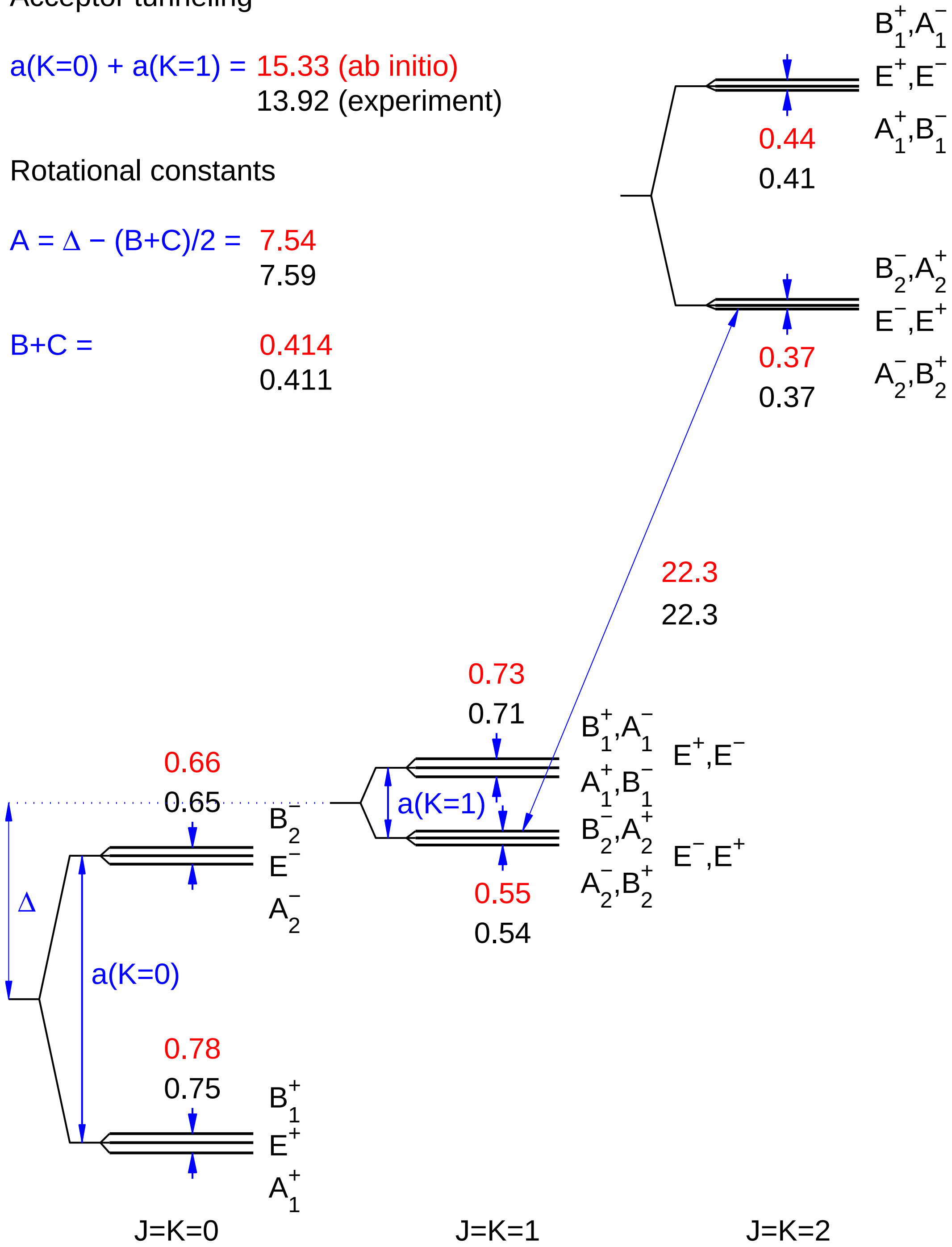
Acceptor tunneling

a(K=0) + a(K=1) = 15.33 (ab initio)
13.92 (experiment)

Rotational constants

A = Δ − (B+C)/2 = 7.54
7.59

B+C = 0.414
0.411



D_2O dimer tunneling levels from CC-pol-8s potential and experiment

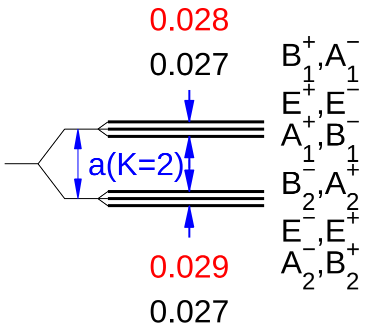
Acceptor tunneling

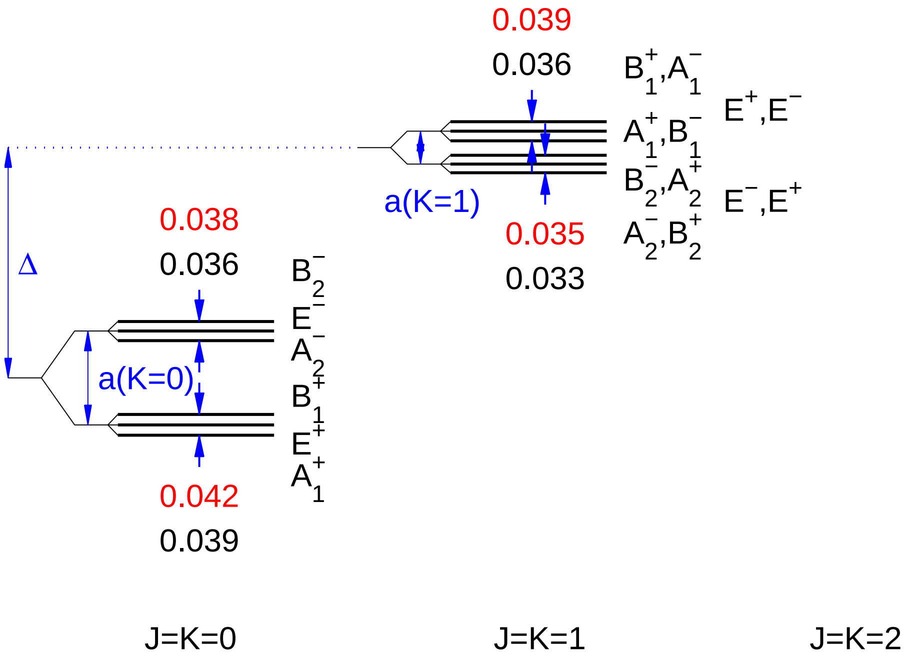
a(K=0)	a(K=1)	a(K=2)	
2.04	0.64	1.48	(ab initio)
1.77	0.62	1.31	(experiment)

Rotational constants

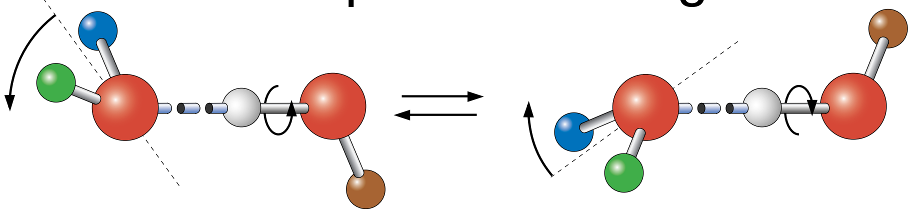
$A = \Delta - (B+C)/2 =$ 4.20
4.17

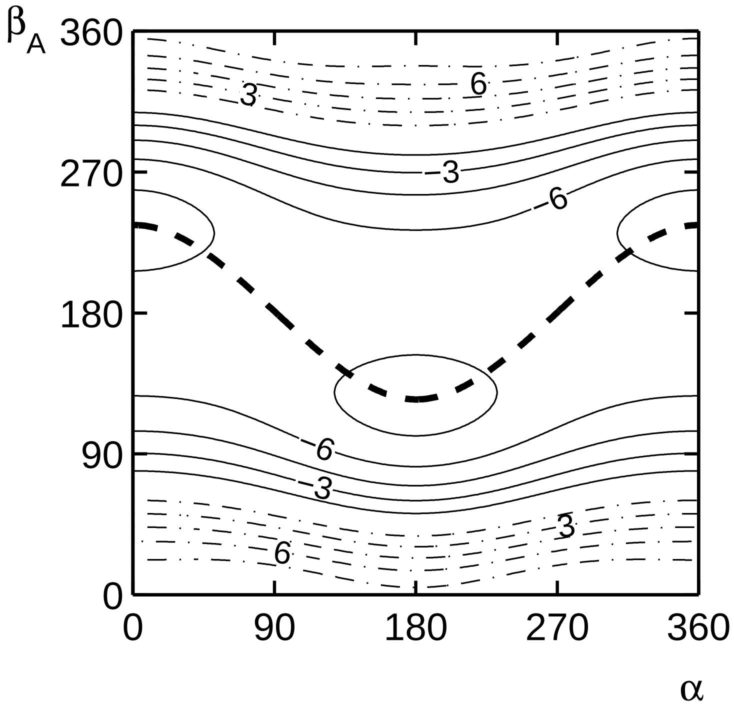
$B+C =$ 0.361
0.362





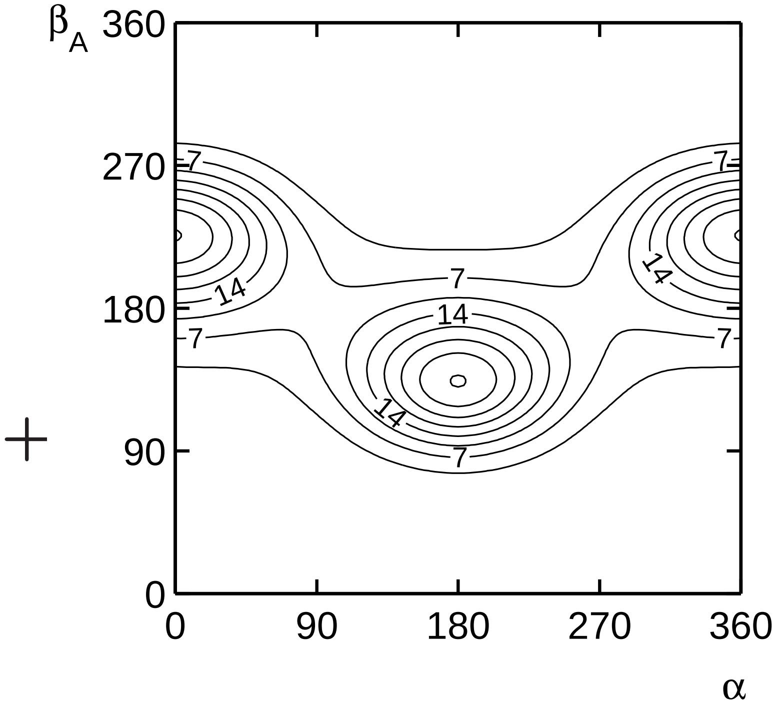
Acceptor Tunneling



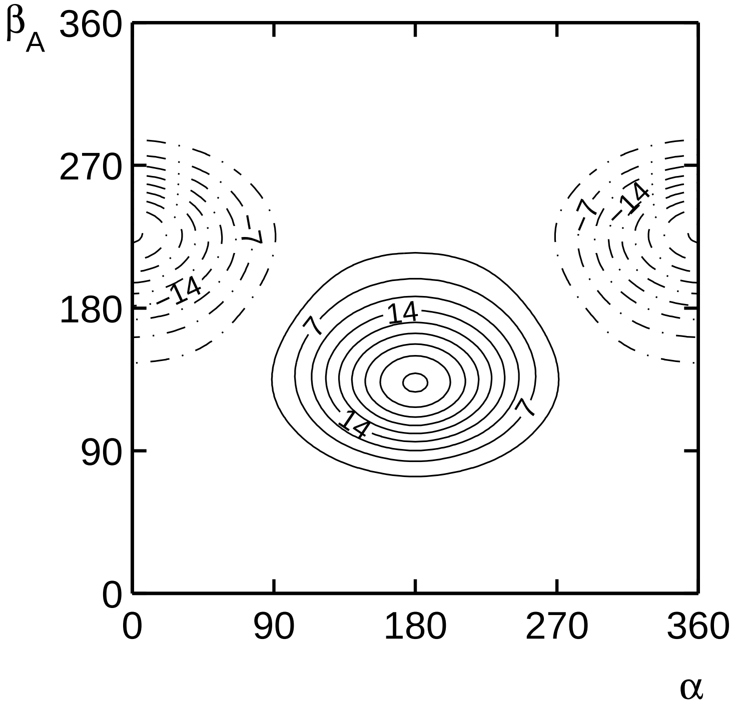


potential

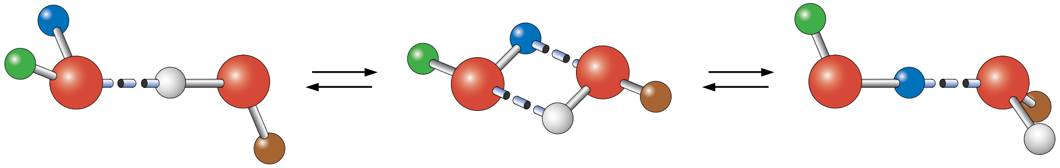
A_1^+, B_1^+, E^+

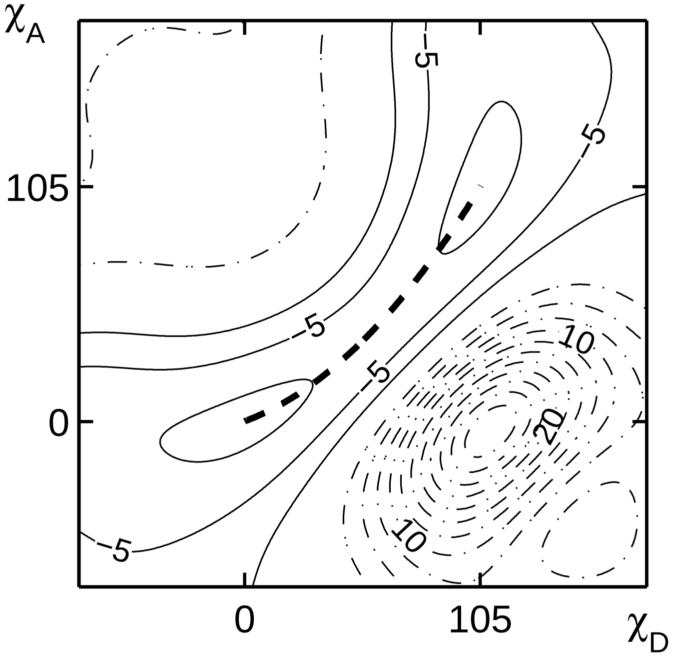


A_2^-, B_2^-, E^-



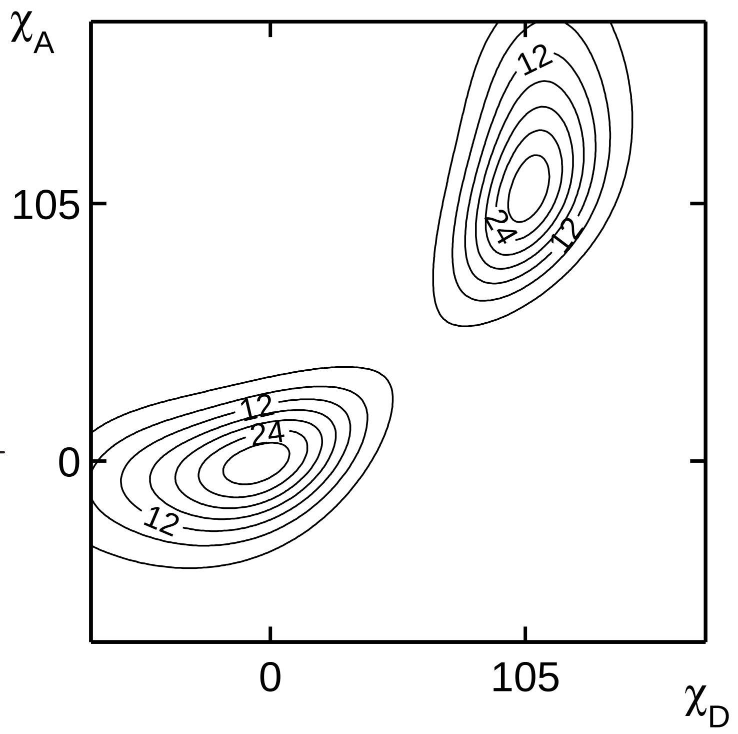
Donor-Acceptor Interchange Tunneling



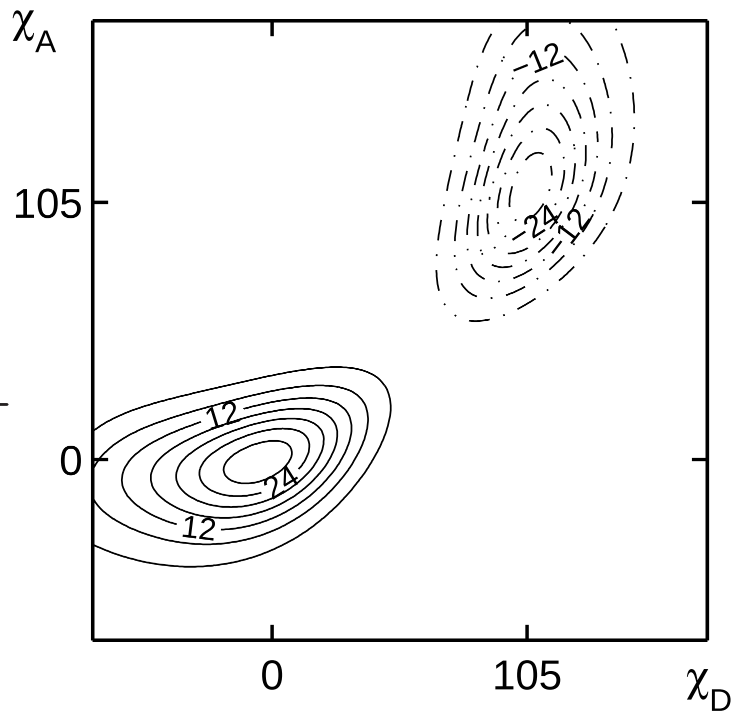


potential

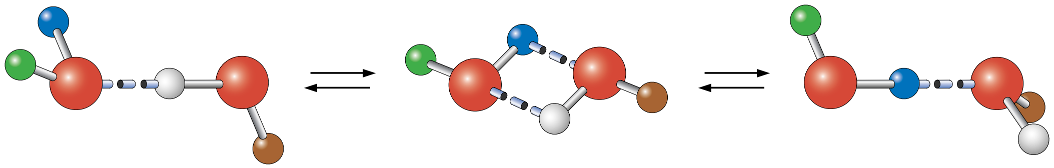
A_1^+ / A_2^-

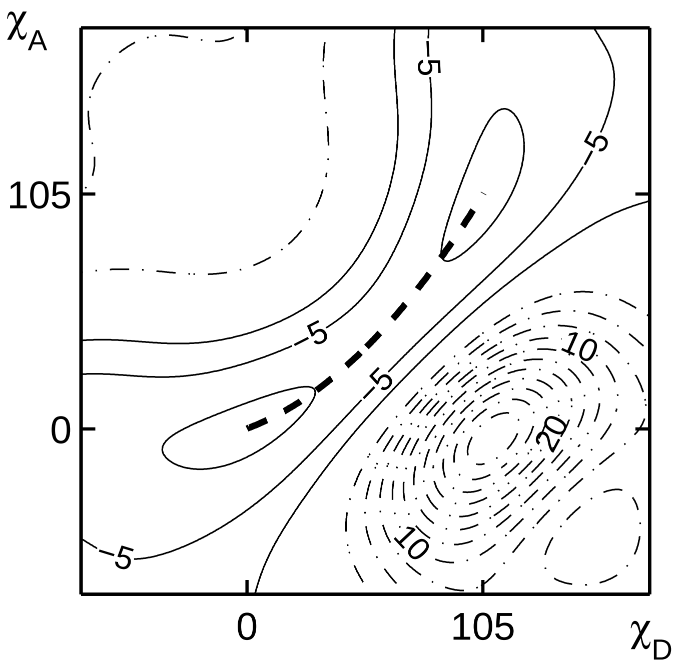


B_1^+ / B_2^-

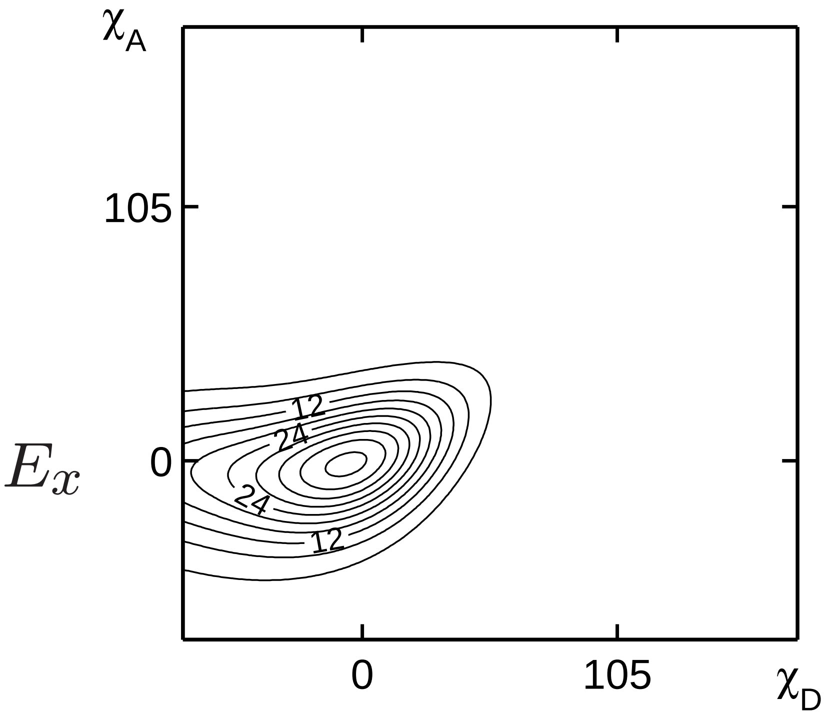


E states localized

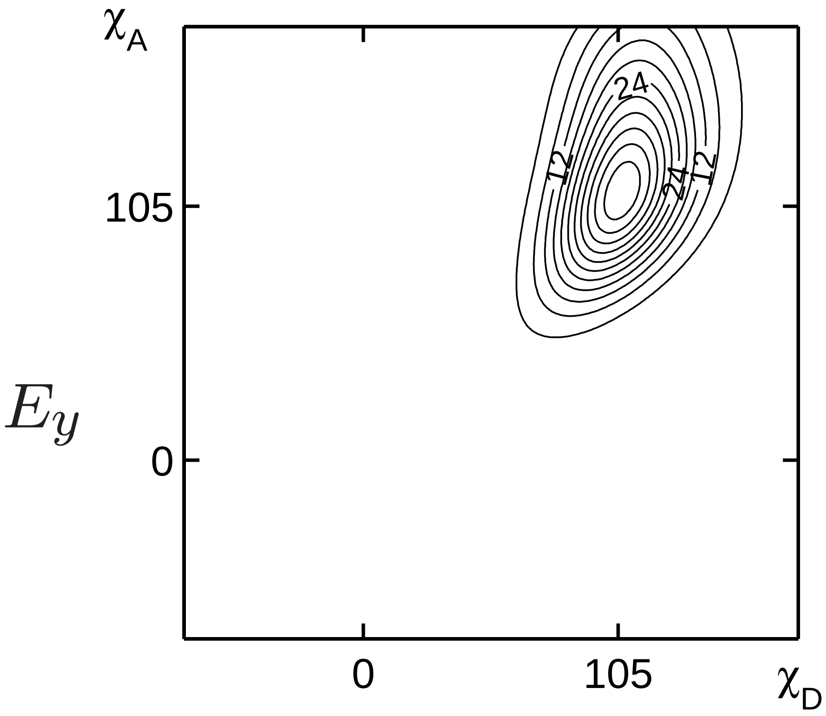




potential

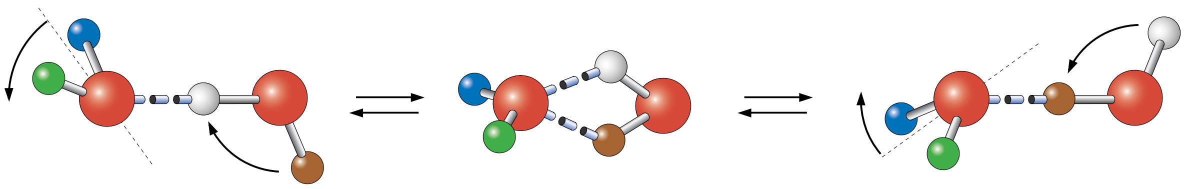


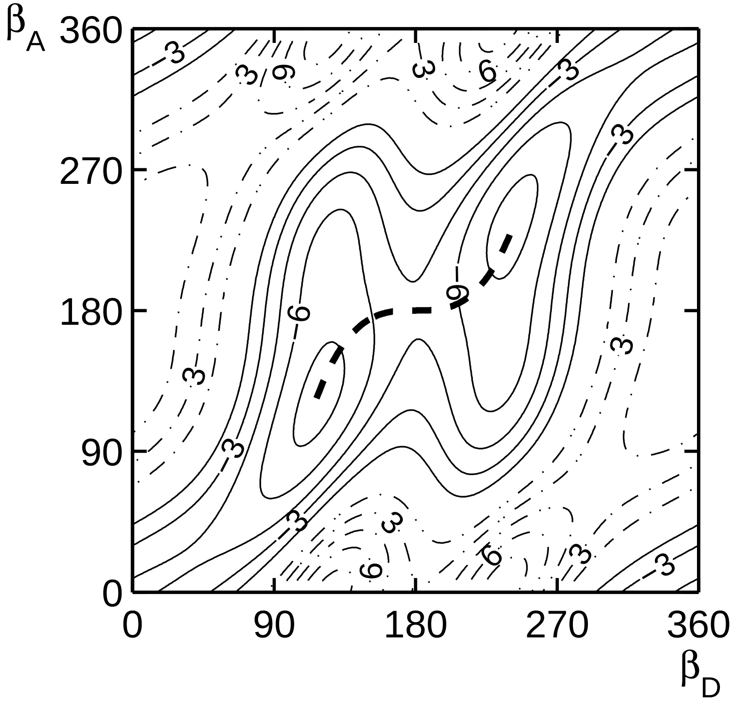
E_x



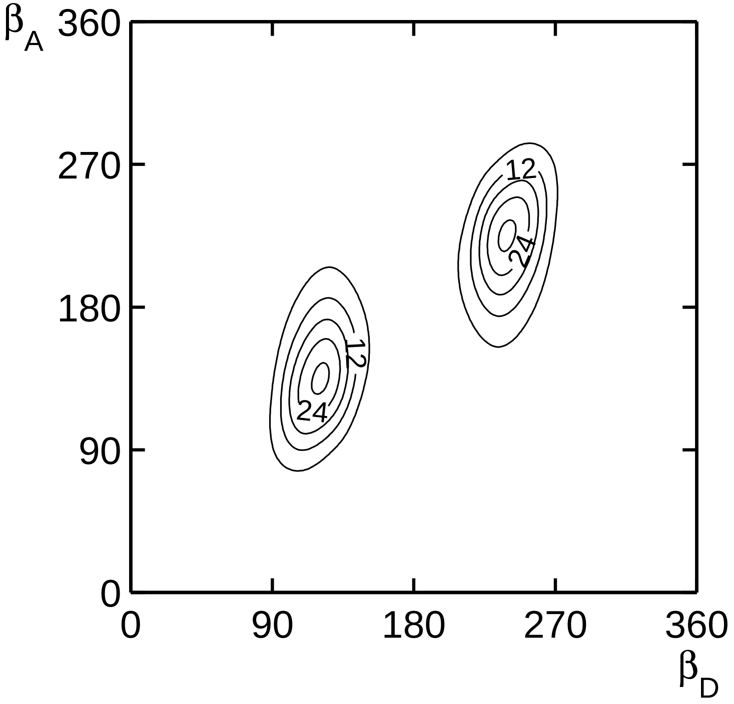
E_y

Donor (Bifurcation) Tunneling



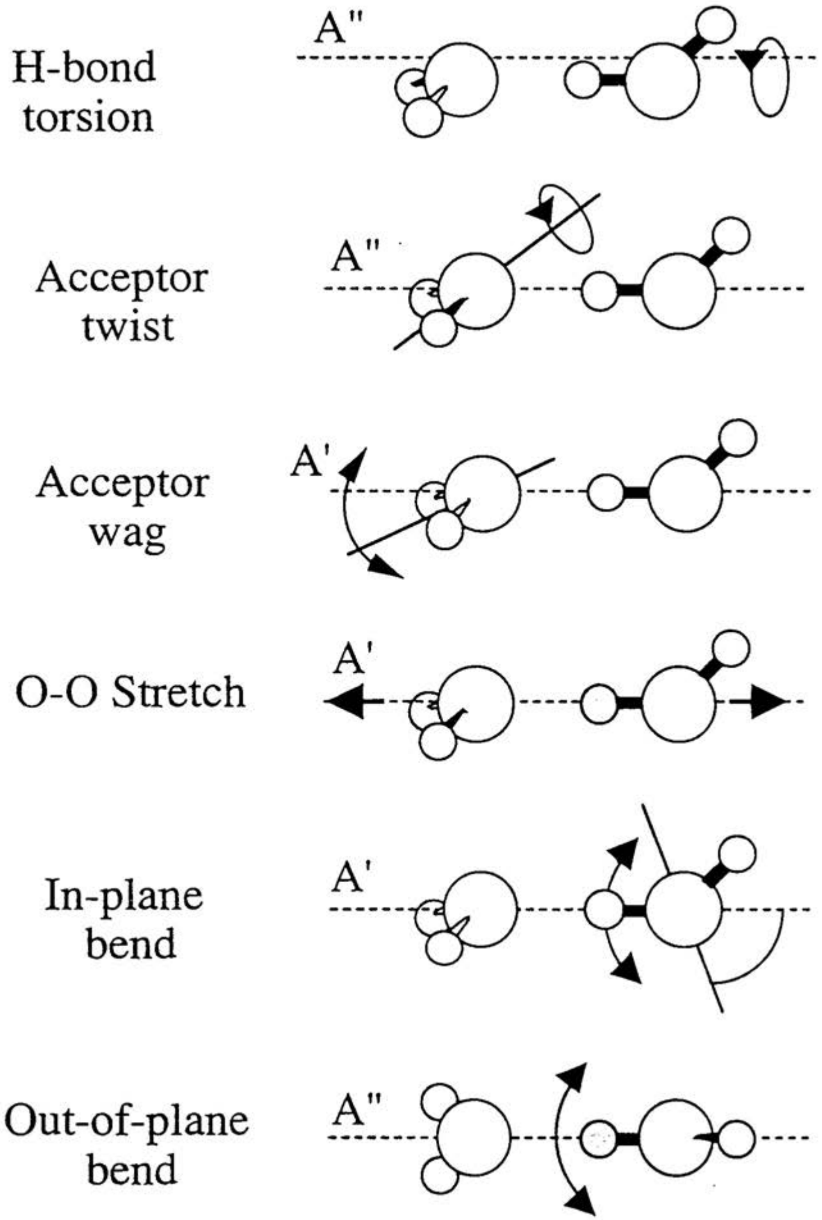


potential

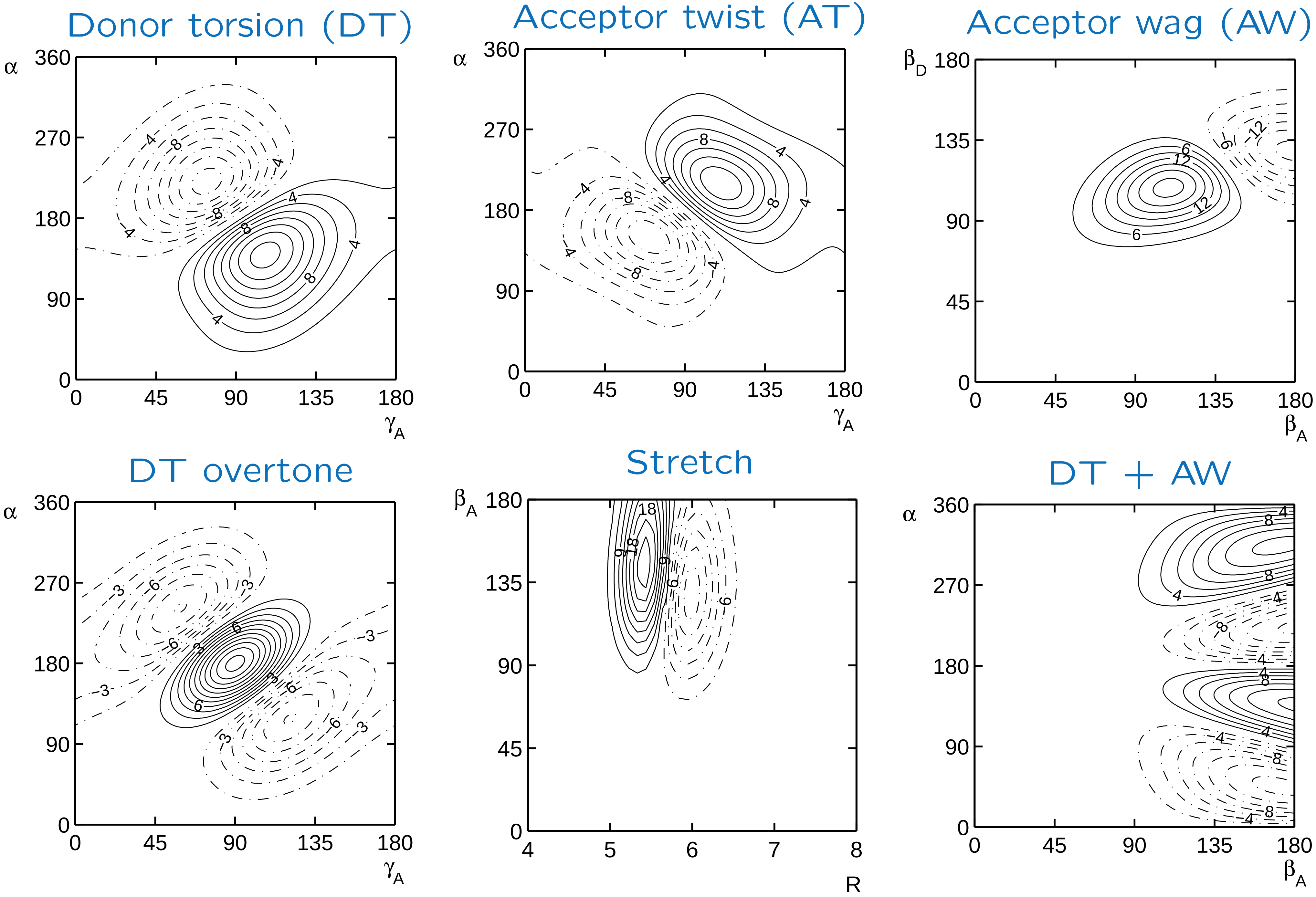


$A_1^+ / B_1^+ / A_2^- / B_2^- / E^+ / E^-$

Intermolecular vibrations



Wave functions



Donor torsion (DT)

Acceptor twist (AT)

Acceptor wag (AW)

DT overtone

Stretch

DT + AW

H_2O dimer

intermolecular

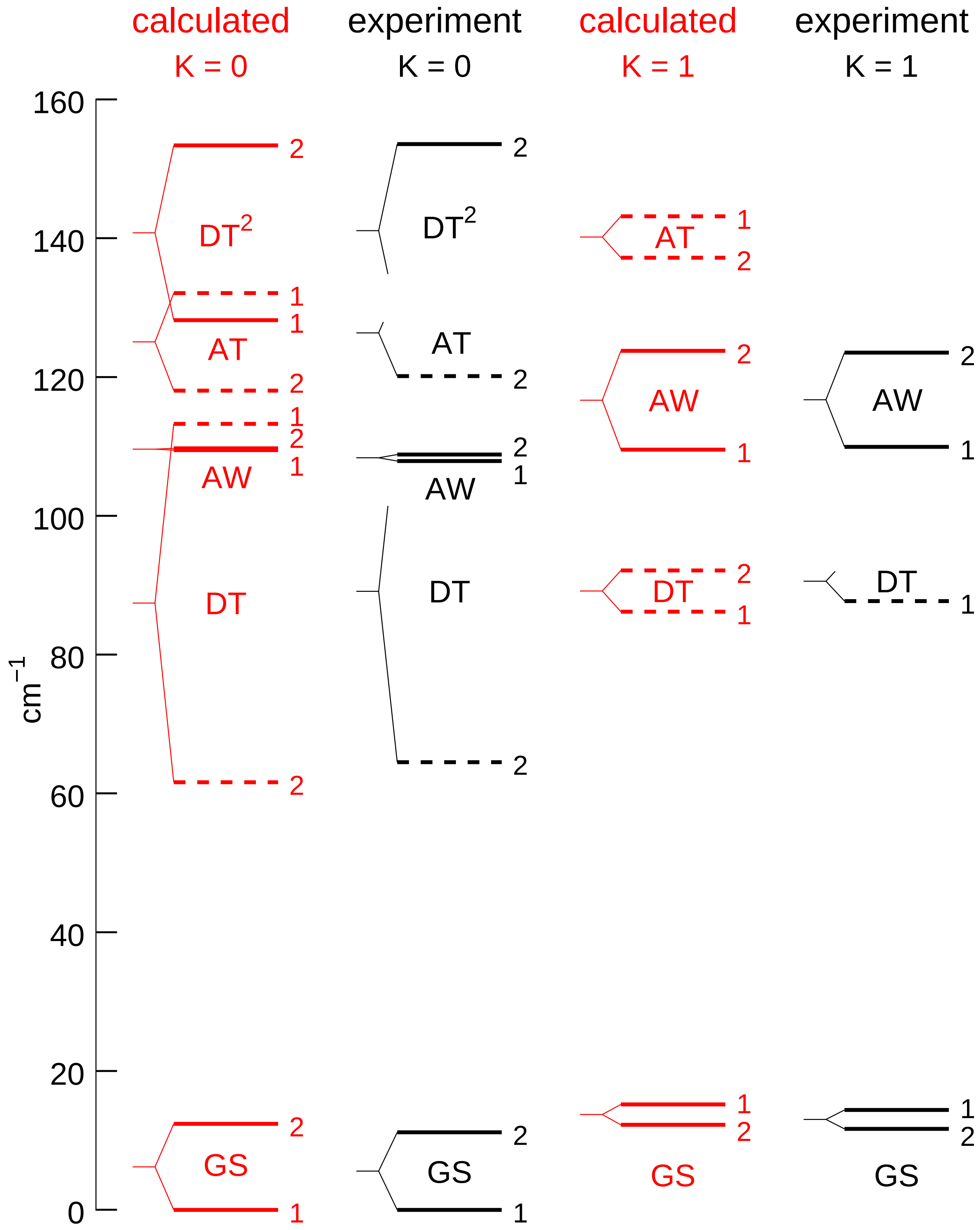
vibrations

from CC-pol-8s

potential

and

experiment



D_2O dimer

intermolecular

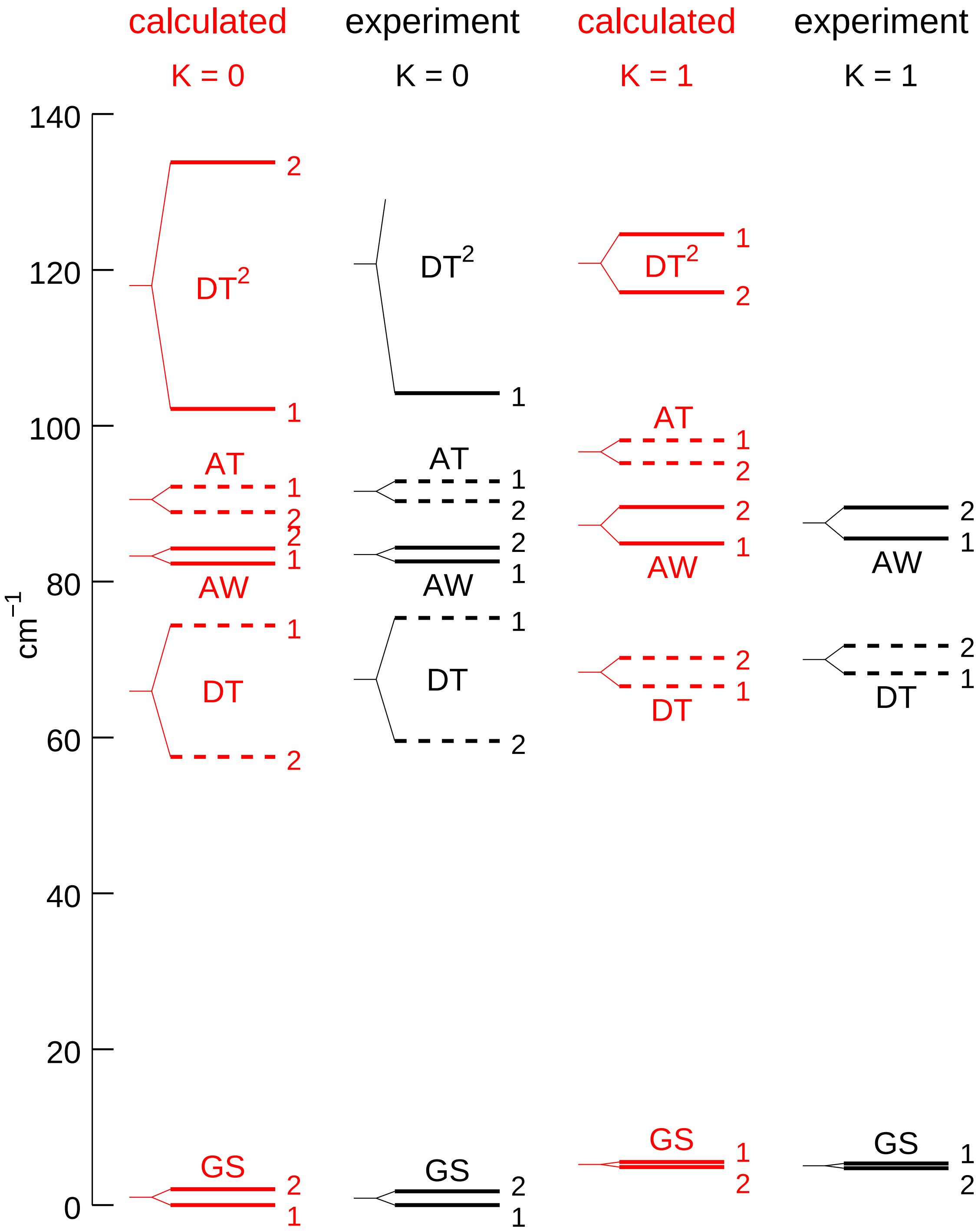
vibrations

from CC-pol-8s

potential

and

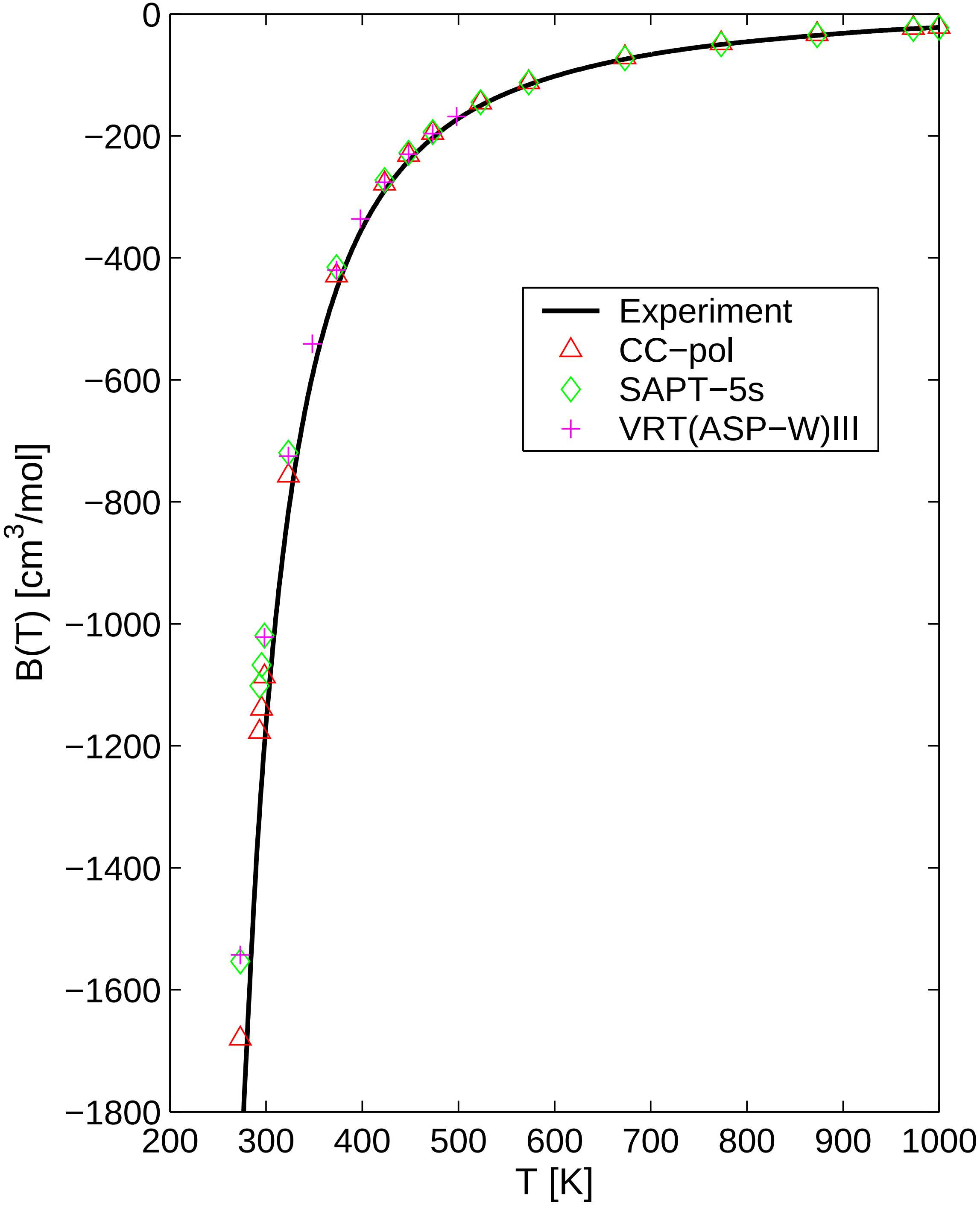
experiment



Second virial

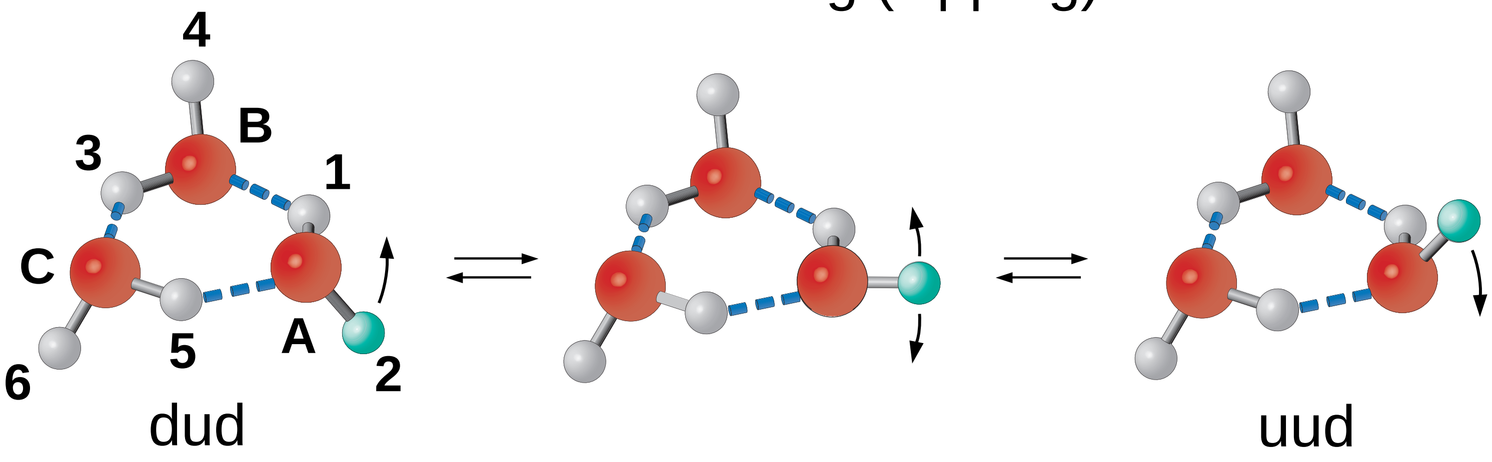
coefficient

of water vapor

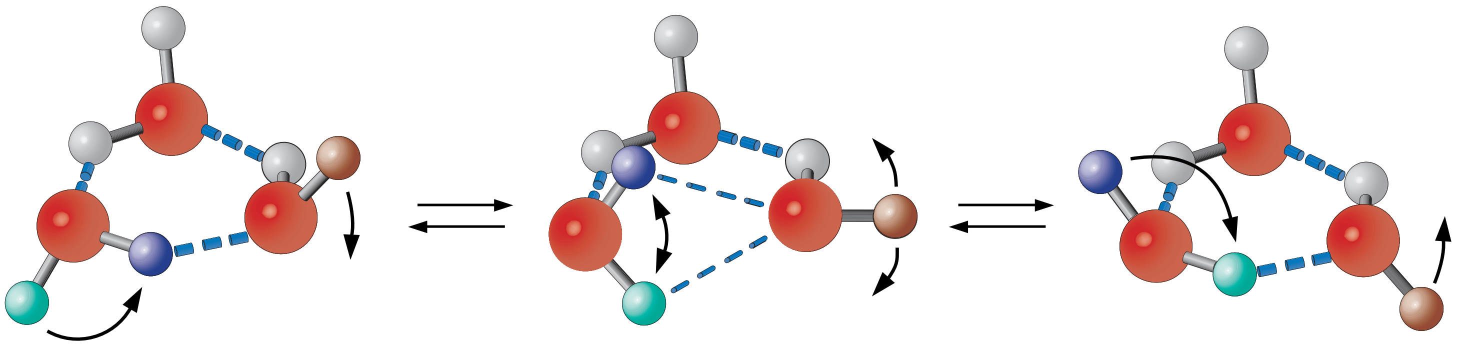


Water trimer tunneling pathways

Torsional tunneling (flipping)



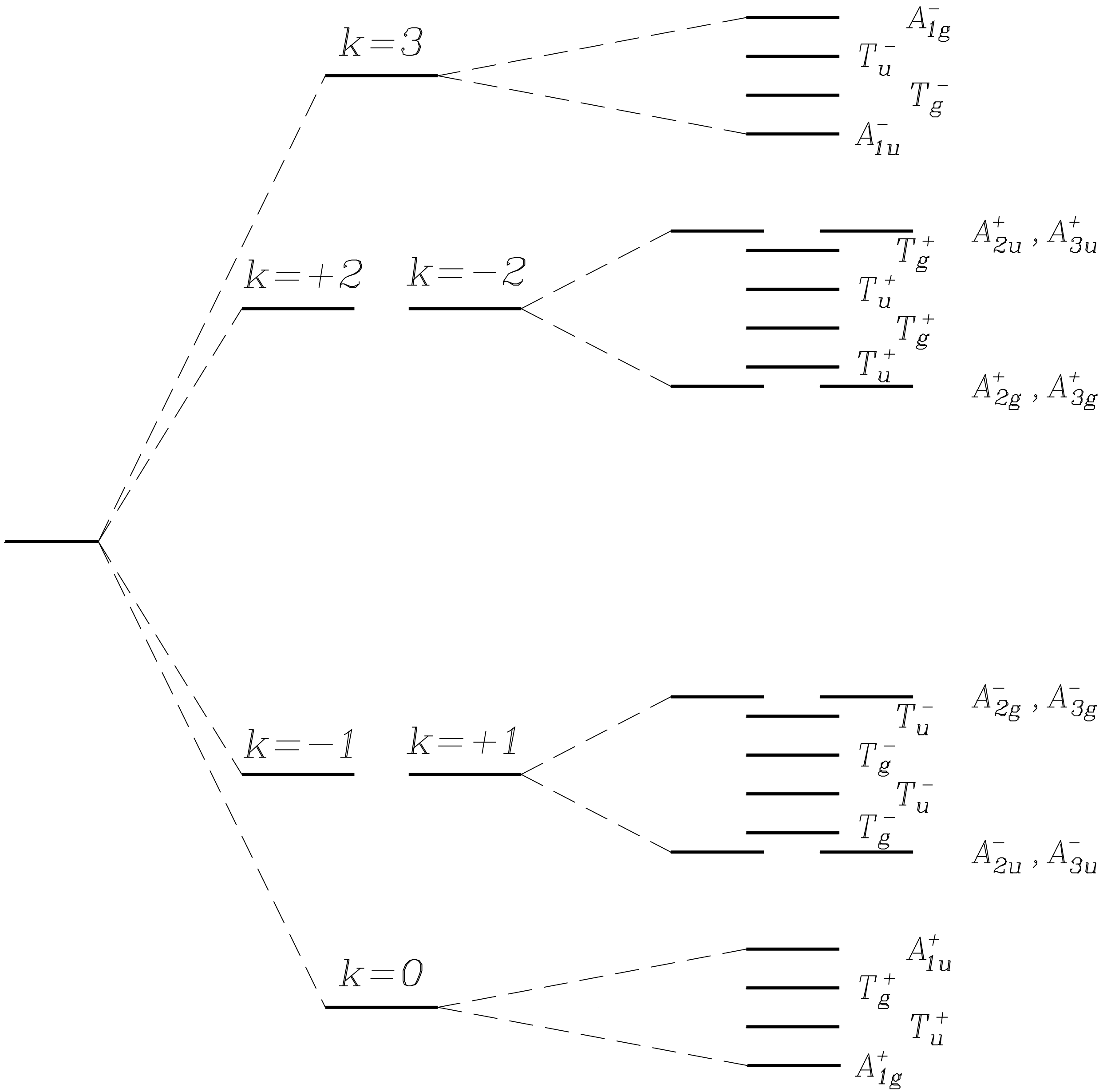
Bifurcation (donor) tunneling

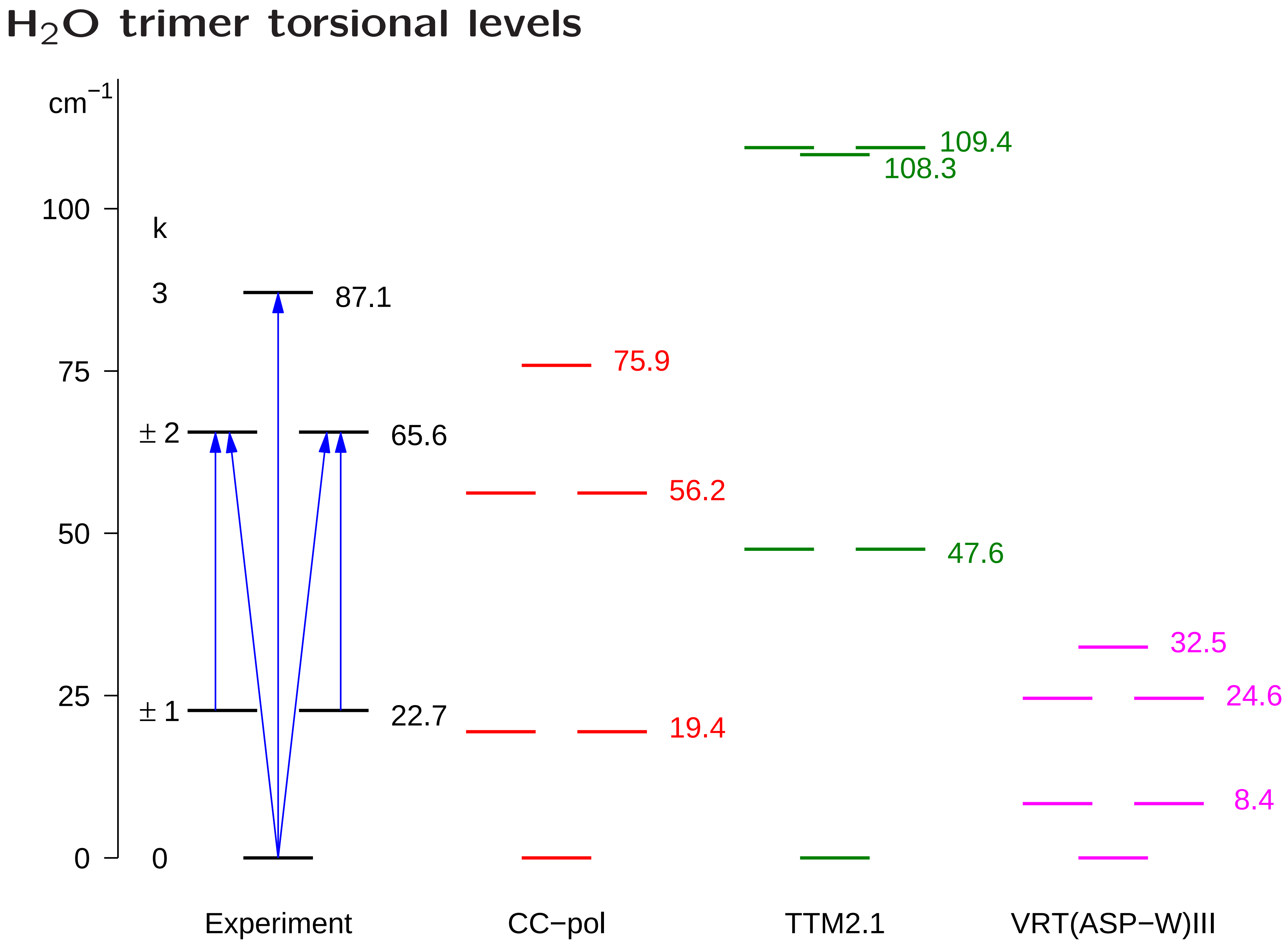


Water trimer tunneling levels

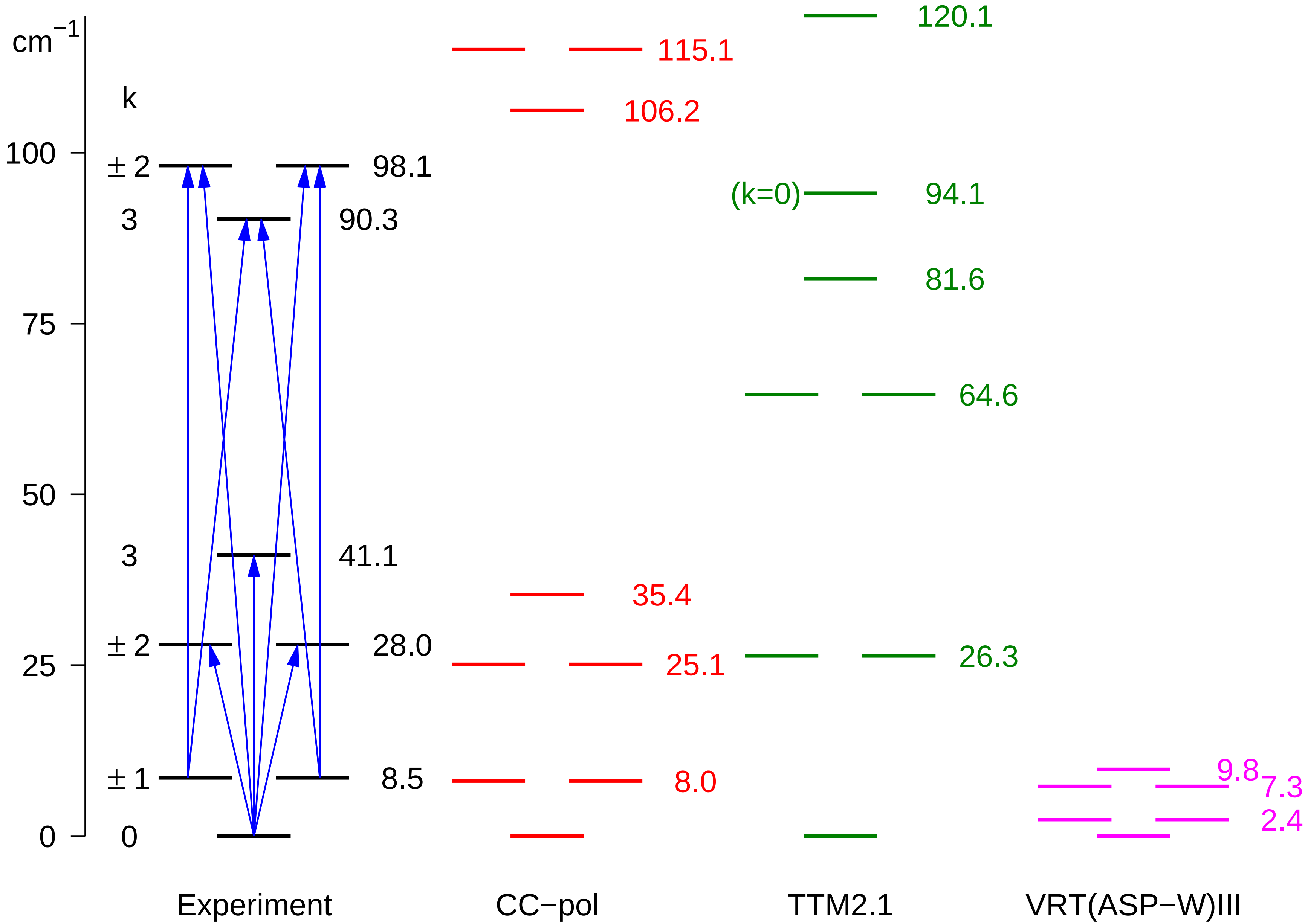
$(J = 0)$

flipping (G_6) + *bifurcation tunneling* (G_{48})

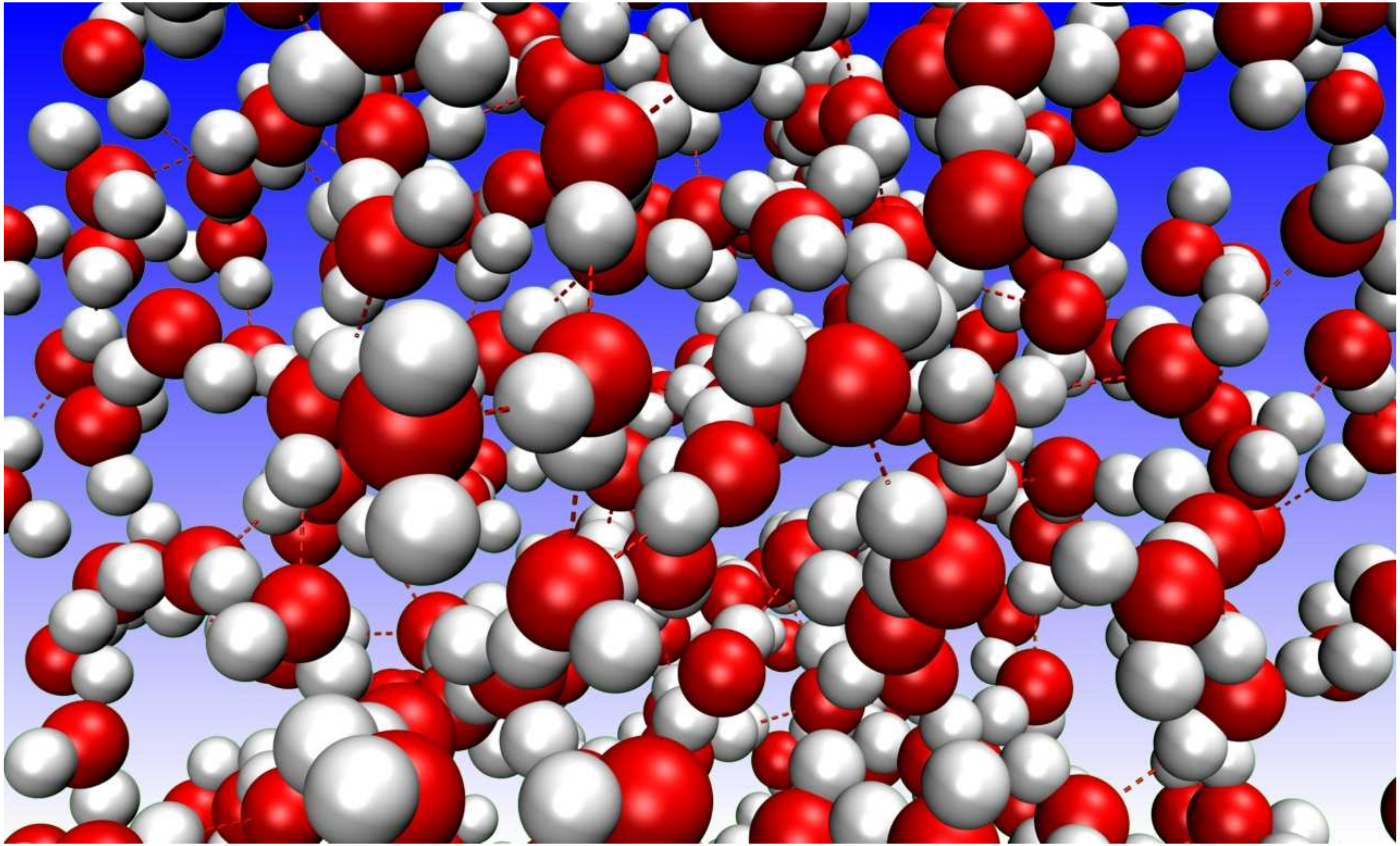


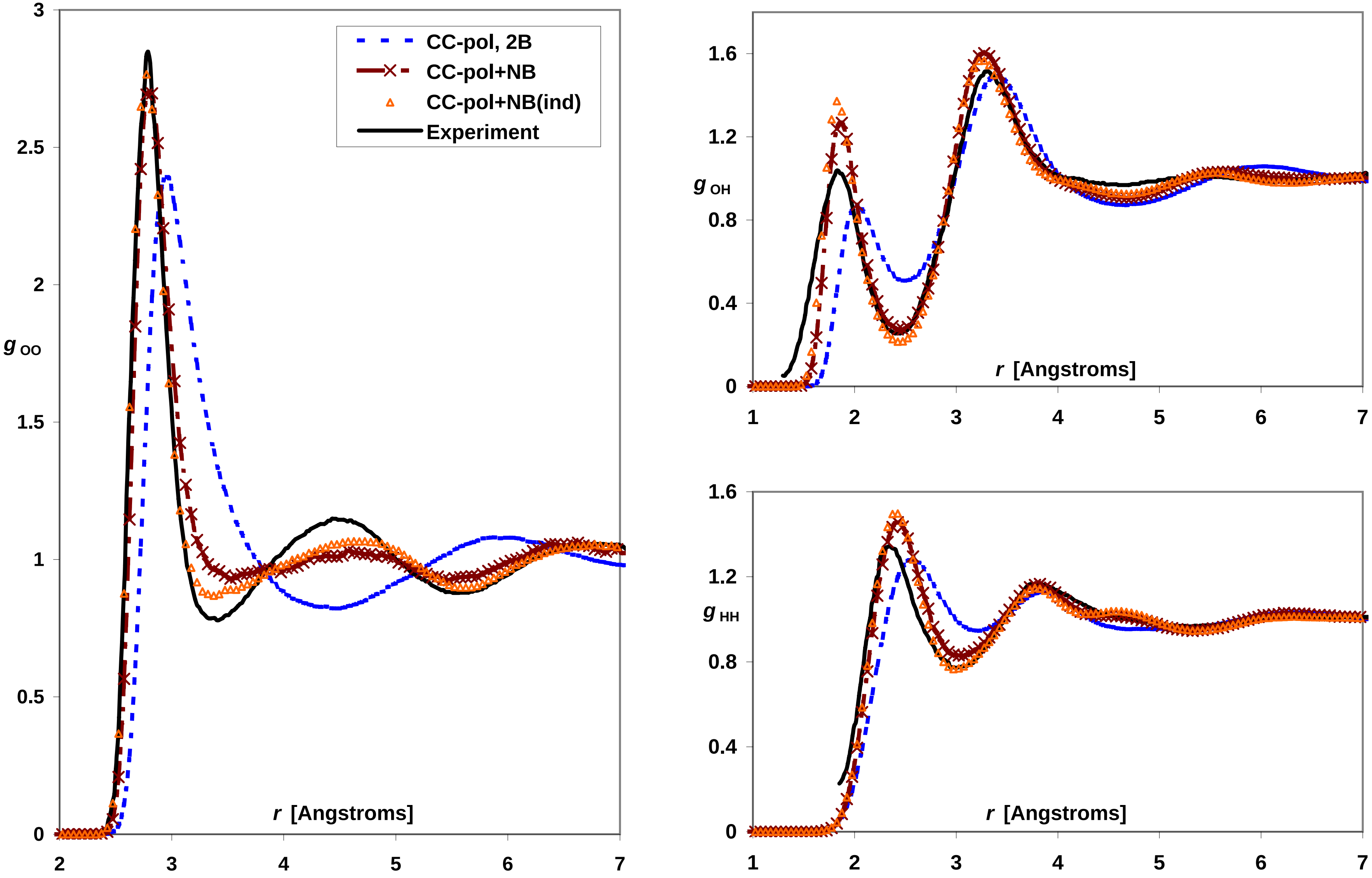

H$_2$O trimer torsional levels
cm^{-1}
100
75
50
25
0
k
3
± 2
± 1
0
87.1
65.6
22.7
75.9
56.2
19.4
109.4
108.3
47.6
32.5
24.6
8.4
Experiment
CC−pol
TTM2.1
VRT(ASP−W)III

D_2O trimer torsional levels



MD simulations of liquid water, T = 298 K





Atom-atom radial distribution functions

Conclusions

- CC-pol pure *ab initio*
- Predicts dimer spectra better than semi-empirical potentials fitted to these spectra
- Second virial coefficients in excellent agreement with experiment
- CC-pol + 3-body potential gives good trimer spectrum
- Simulations of liquid water with CC-pol + N-body forces predict the neutron and X-ray diffraction data equally well as the best empirical potentials fitted to these data
- Important role of many-body forces in liquid water

  Nearly tetrahedral coordination:

  3.8 hydrogen bonds, only 2.8 with pure pair potential

General conclusion

CC-pol, with the accompanying many-body interaction model, provides the first water force field that recovers the dimer, trimer, and liquid properties well

Resonances (quasi-bound states)

in molecular collisions

Why are resonances important?

See: D. W. Chandler, J. Chem. Phys, **132**, 110901 (2010)
on shape/orbiting resonances:

- Long life time of collision complex
- Enable recombination reactions A + B → AB
- Probe long range behavior of the potential

Early (1972-1979) observations in scattering for H-Hg by Scoles *et al.* and for H-X, H_2-X with X = Ar, Kr, Xe by Toennies *et al.* ($E \geq 8$ cm^{-1})

Also observed in dimer spectra, e.g. for He-HF by Nesbitt *et al.*

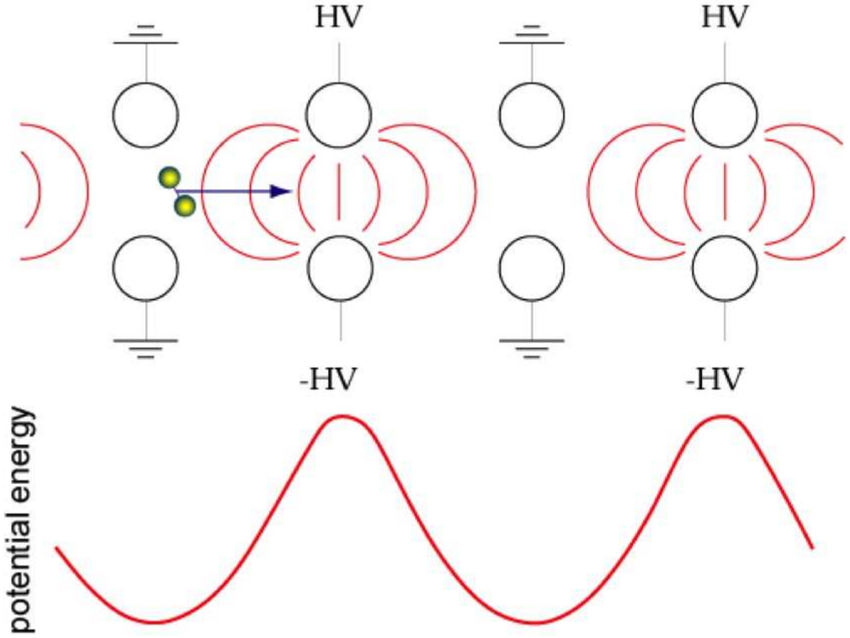
Anomalous line broadening seen in Ar-CH_4 by Roger Miller, due to resonances, explained by calculations of AvdA *et al.*

Difficult to observe resonances in molecular (crossed) beam scattering experiments

- Collision energies too high
- Difficult to scan the collision energy
- Energy spread too large $\Rightarrow$ too much averaging

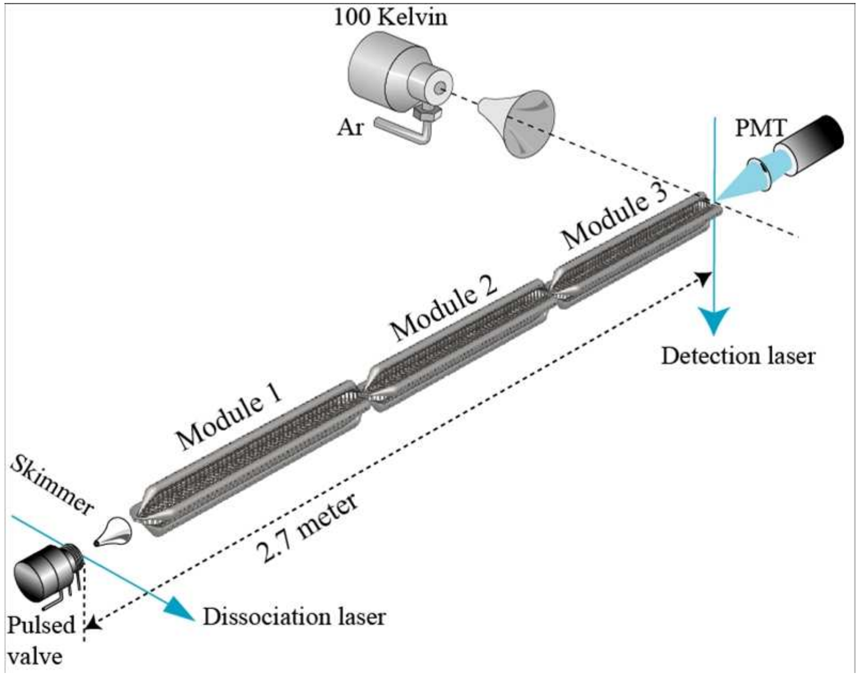
New possibilities:

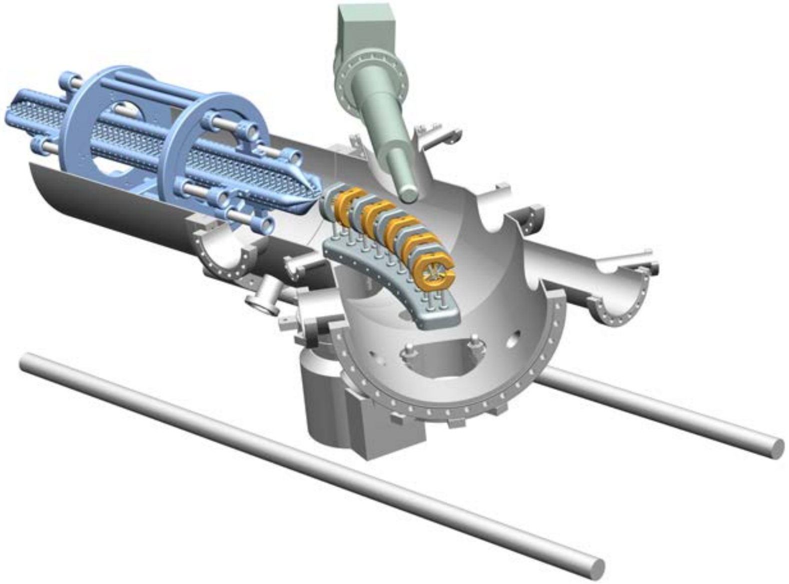
Stark-decelerated molecular beams ⇒ velocity-tuning and state-selection



Gerard Meijer, Berlin

Crossed beam setups

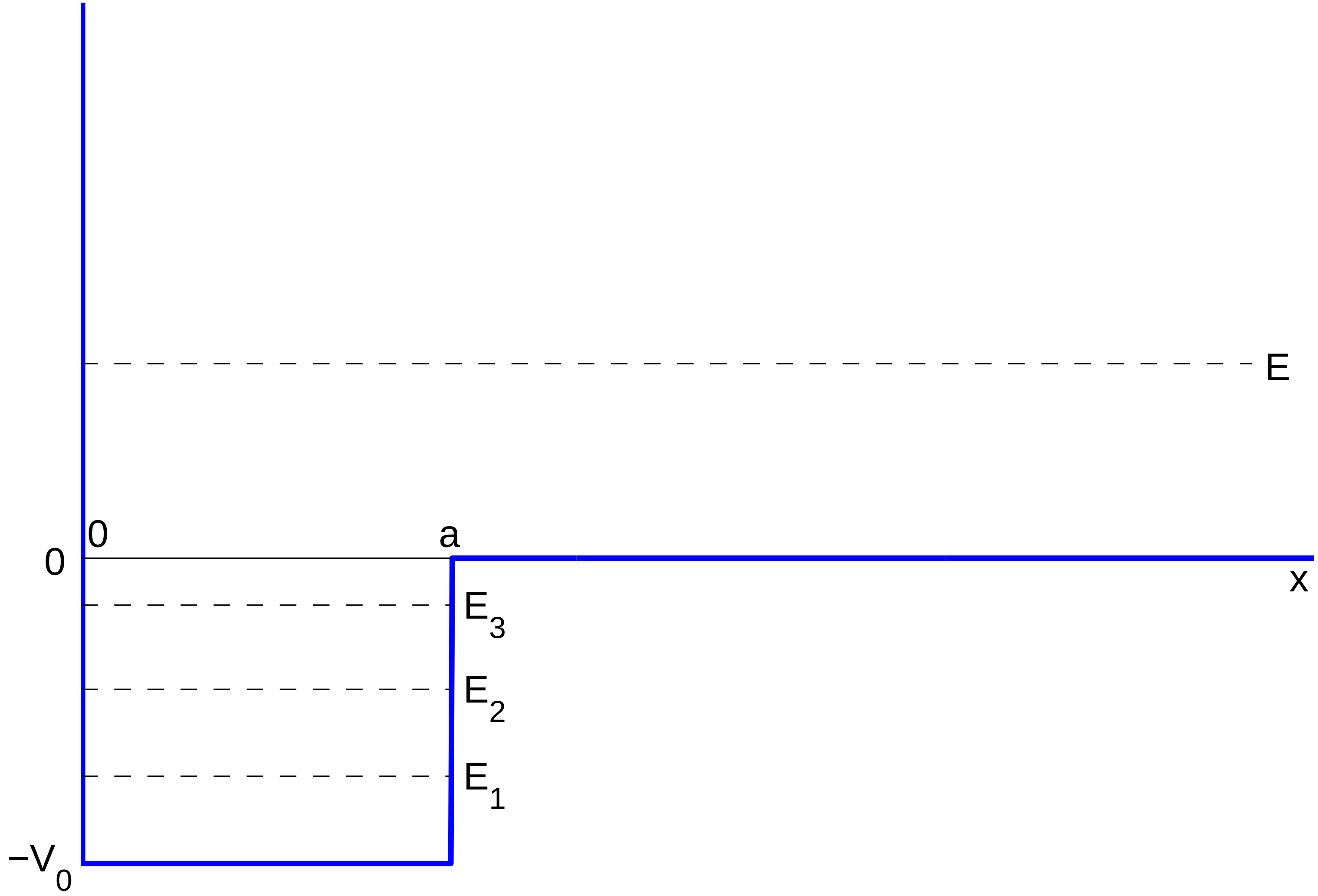




Bas van de Meerakker, Gerard Meijer: Berlin/Nijmegen

Textbook example of scattering resonances

Square well potential



Scattering wave function at energy E

$$\psi \;=\; \begin{cases} 2\,A\,e^{i\varphi}\sin(k_0 x) & \text{for } 0 \le x \le a, \;\text{ with } k_0 = \sqrt{2m(E+V_0)} \\ e^{-ikx} + e^{i(kx+2\varphi)} & \text{for } a < x, \qquad\quad \text{with } k = \sqrt{2mE} \end{cases}$$

Match functions and log-derivatives at $x = a$

Phase shift

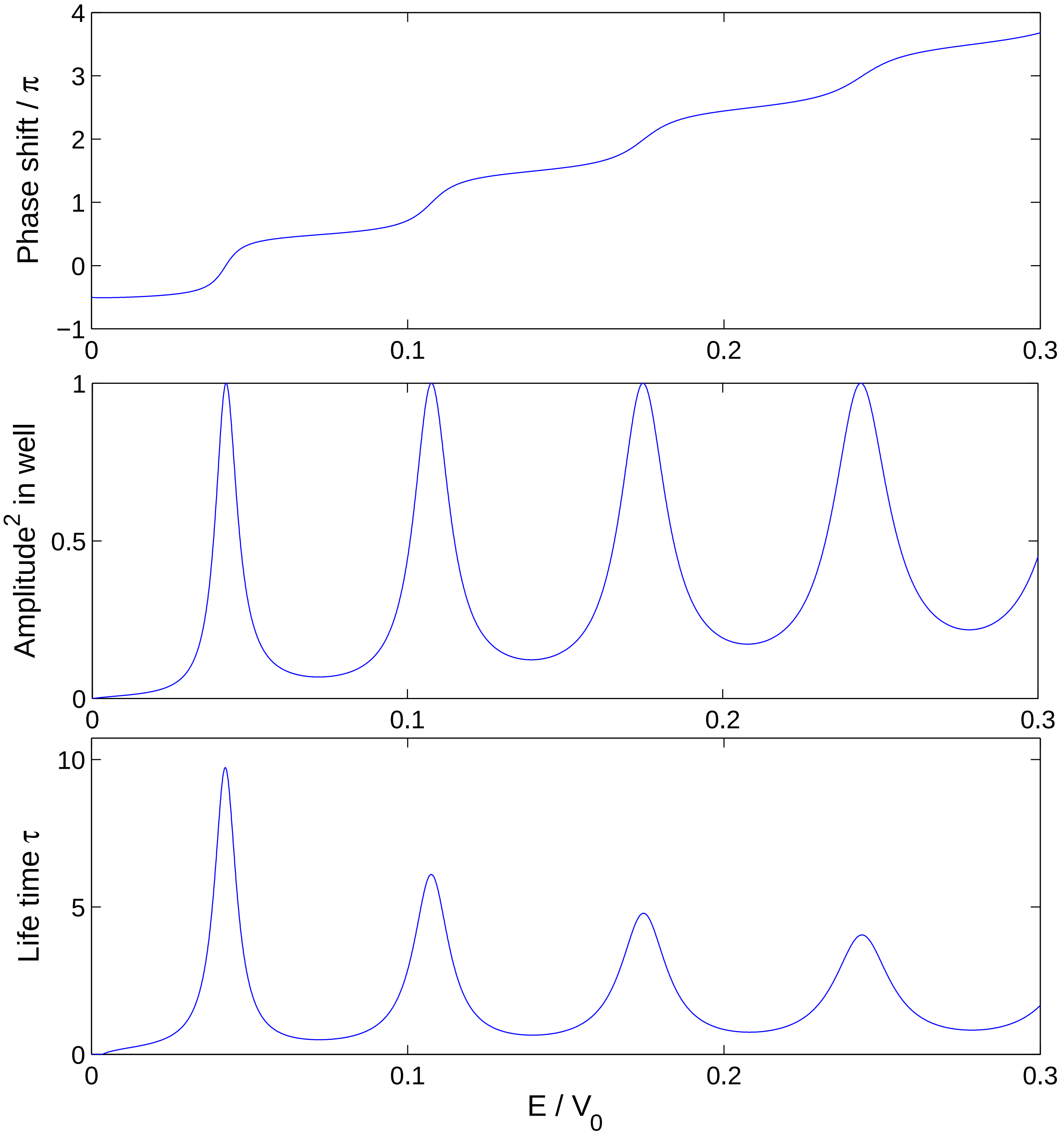
$$\varphi = \arctan\left[\frac{k}{k_0}\tan\left(k_0 a\right)\right] - \frac{\pi}{2}$$

Weight in well region

$$A^2 = \frac{k^2}{k^2 + V_0\cos^2(k_0 a)}$$

Life time

$$\tau = \frac{1}{v}\frac{\partial\varphi}{\partial k} = \frac{\partial\varphi}{\partial E}$$



Phase shift / π
4
3
2
1
0
−1
0
0.1
0.2
0.3
Amplitude^2 in well
1
0.5
0
0
0.1
0.2
0.3
Life time τ
10
5
0
0
0.1
0.2
0.3
E / V_0

Molecule-molecule collisions, theory

- Use same Hamiltonian as in bound state calculation on dimers
- Use same angular basis
- Instead of using radial basis, solve coupled differential equations in R by propagator method (log-derivative, Numerov, Airy, etc.)

Time independent quantum scattering theory

Channels, molecule-molecule (asymptotic, uncoupled)

$$|\,\boldsymbol{n}\,\rangle = |\,v_A j_A m_A k_A\,\rangle\,|\,v_B j_B m_B k_B\,\rangle$$

Plane wave in center-of-mass frame

$$\Psi_{\boldsymbol{n}}^{\mathrm{pw}} = |\,\boldsymbol{n}\,\rangle e^{i\boldsymbol{k_n}\cdot\boldsymbol{R}}, \quad E = \frac{\hbar^2 k_{\boldsymbol{n}}^2}{2\mu} + \epsilon_{\boldsymbol{n}}, \quad \boldsymbol{k_n} = k_{\boldsymbol{n}}\widehat{\boldsymbol{k}}$$

Expansion in spherical waves for large R

$$e^{i\boldsymbol{k_n R}} = \frac{2\pi}{ik_{\boldsymbol{n}}}\sum_{LM_L} Y_{LM_L}(\widehat{\boldsymbol{R}})\frac{e^{i(k_{\boldsymbol{n}}R-L\frac{\pi}{2})} - e^{-i(k_{\boldsymbol{n}}R-L\frac{\pi}{2})}}{R} i^L Y_{LM_L}(\widehat{\boldsymbol{k}})^*$$

Coupled channels method

Expand wave function in $|\,\boldsymbol{n}LM_L\,\rangle = |\,\boldsymbol{n}\,\rangle Y_{LM_L}(\widehat{\boldsymbol{R}})$

$$\Psi_{\boldsymbol{n}LM_L} = \frac{1}{R}\sum_{\boldsymbol{n}'L'M_L'} |\,\boldsymbol{n}'L'M_L'\,\rangle\, U_{\boldsymbol{n}'L'M_L';\boldsymbol{n}LM_L}(R)$$

Substitution into Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}R^{-1}\frac{d^2}{dR^2}R + \Delta H - E\right)\Psi_{\boldsymbol{n}LM_L} = 0$$

yields matrix problem

$$\boldsymbol{U}''(R) = \boldsymbol{W}(R)\,\boldsymbol{U}(R)$$

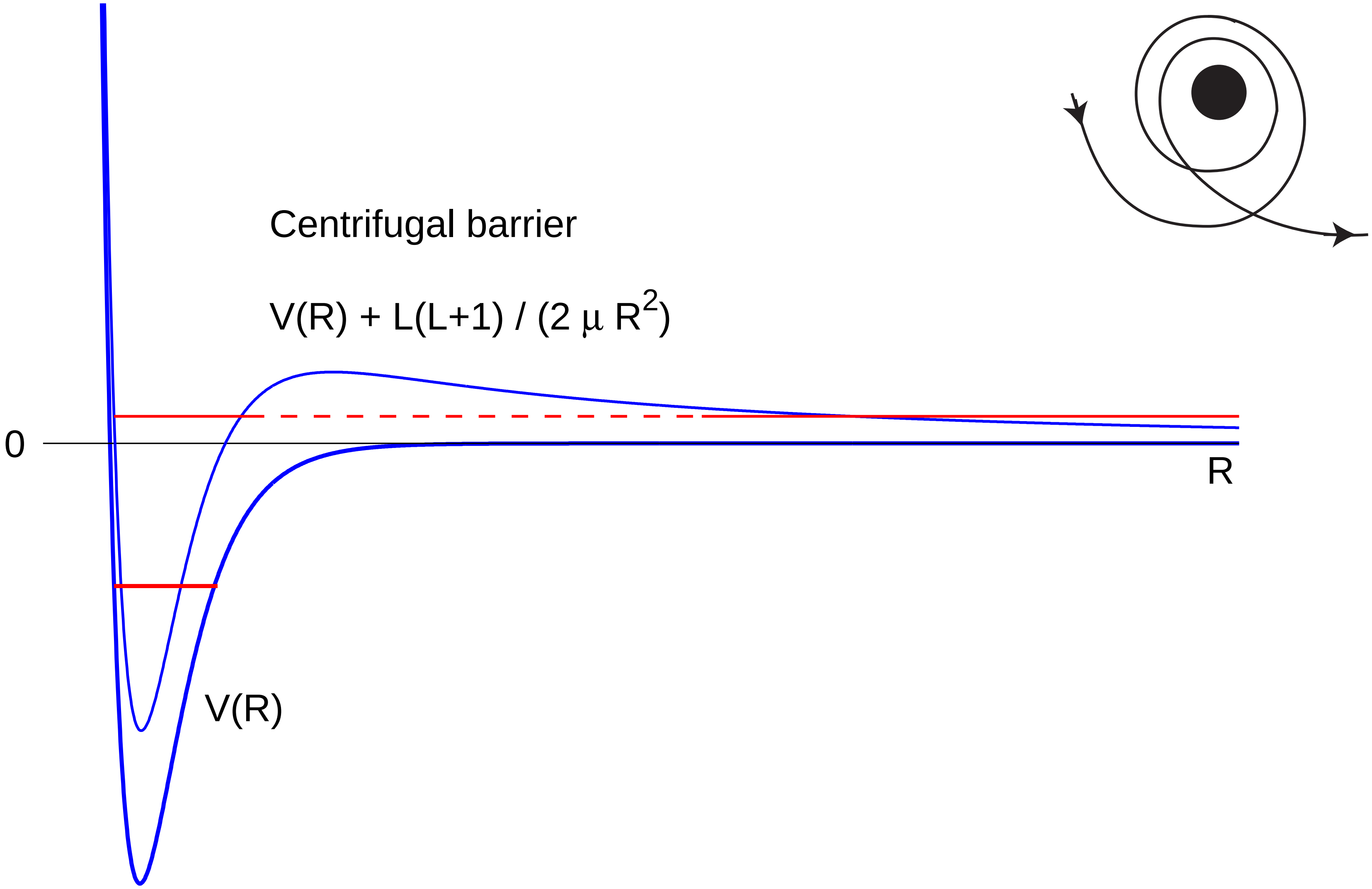
Coupling matrix

$$\boldsymbol{W}_{\boldsymbol{n}'L'M_L';\boldsymbol{n}LM_L}(R) = \frac{2\mu}{\hbar^2}\langle\,\boldsymbol{n}'L'M_L'\,|\Delta H - E|\,\boldsymbol{n}LM_L\,\rangle$$

Coupled-channel calculations

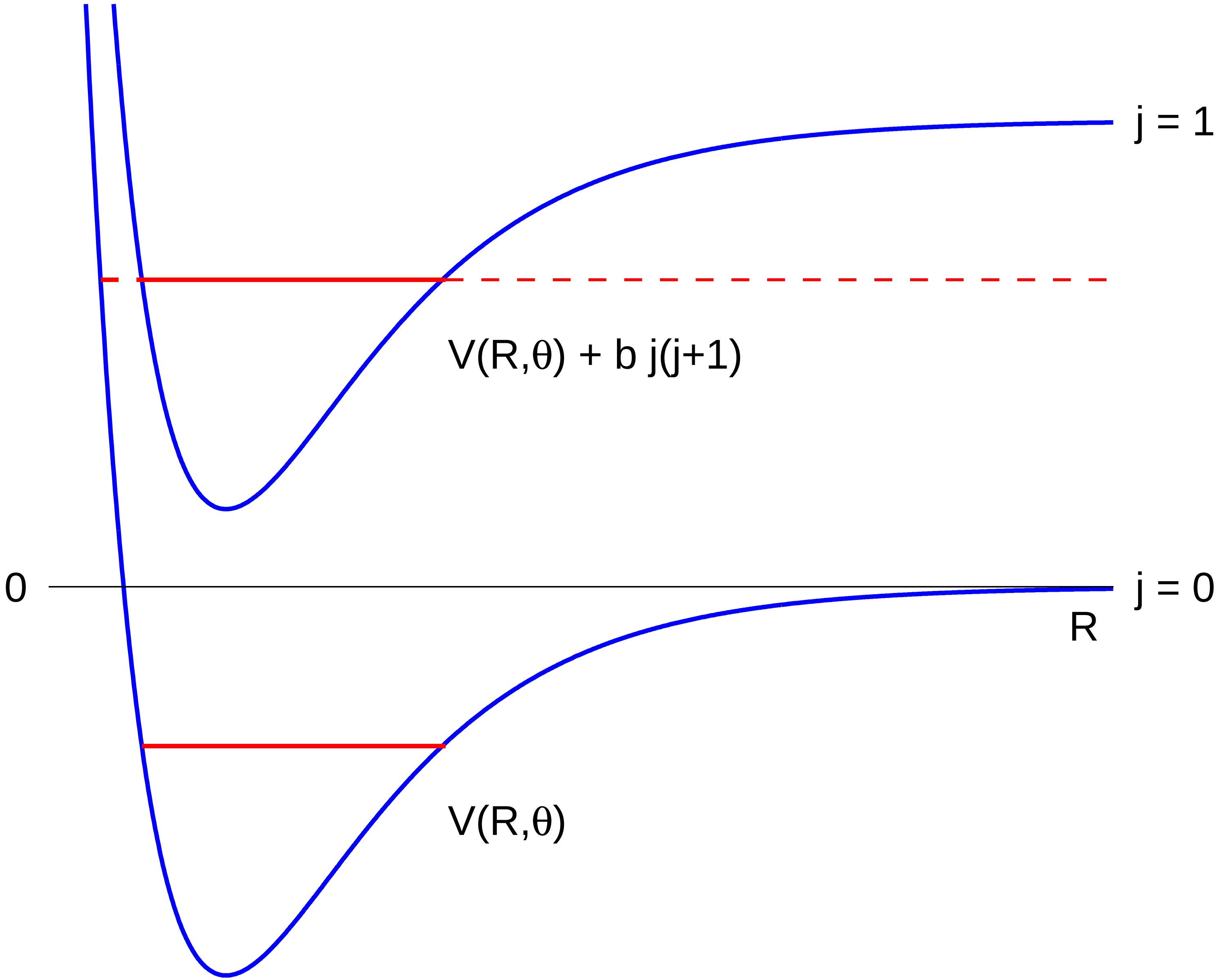
- Solve coupled channel equations $\boldsymbol{U}''(R) = \boldsymbol{W}(R)\,\boldsymbol{U}(R)$ by propagation
- Match $\boldsymbol{U}(R)$ to asymptotic form $\Rightarrow$ S-matrix
- Calculate cross sections, integral and differential
- S-matrix eigenvalues $e^{2i\varphi_j}$ $\Rightarrow$ phase shifts φ_j
- Eigenphase sum $\varphi = \sum_j \varphi_j$, jumps by π at resonances
- Resonance life time $\tau = \frac{1}{v}\frac{\partial\varphi}{\partial k} = \frac{\partial\varphi}{\partial E}$

Shape / orbiting resonances



Feshbach resonances (multichannel)

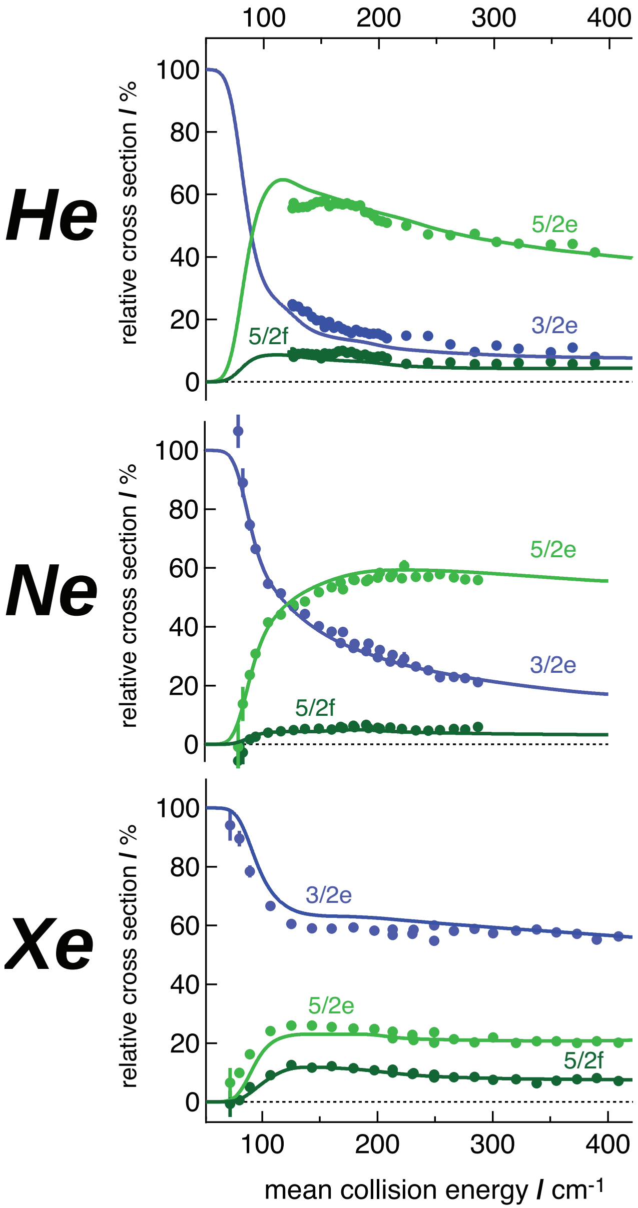
Atom-diatom (j = diatom rotation, b = rotational constant)



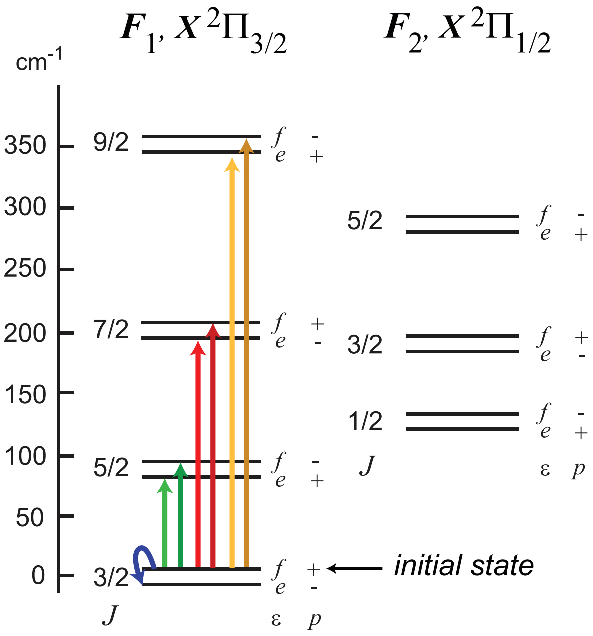
Example 1

OH-X scattering with X = He, Ne, Ar, Kr, Xe

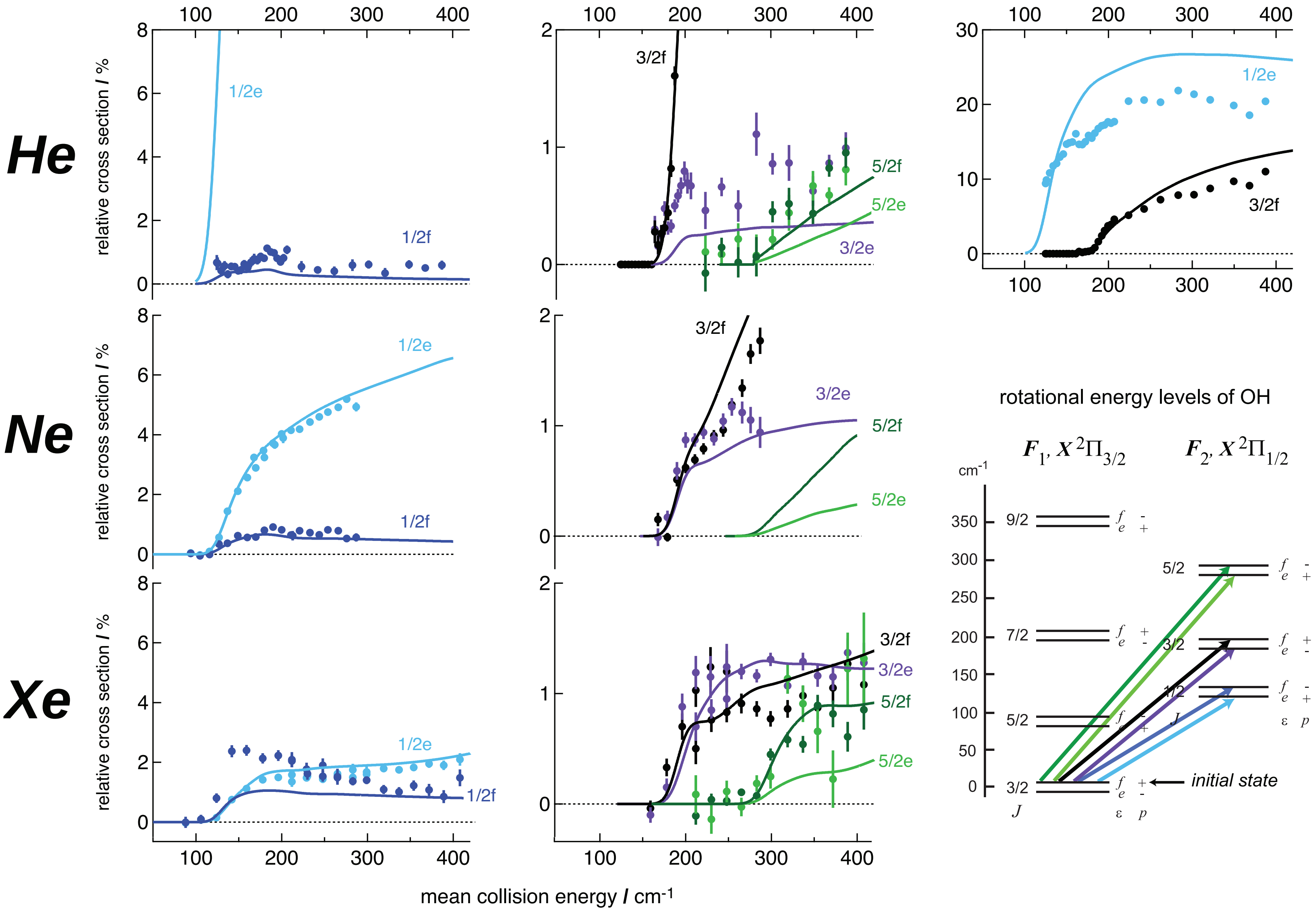
OH-X cross sections



rotational energy levels of OH



More OH-X cross sections

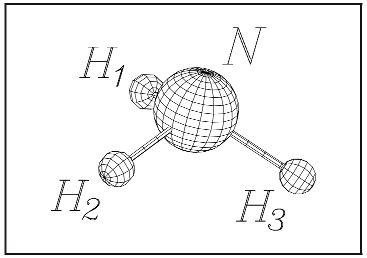
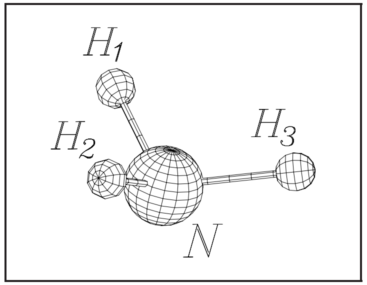


Example 2

NH_3-He scattering

NH_3 monomer

Inversion tunneling (umbrella up ↔ down)

	semi-rigid NH_3	$PI(C_{3v})$ symmetry
	+ inversion tunneling	$PI(D_{3h})$ symmetry also E^* feasible

Rotation-inversion Hamiltonian

$$\begin{aligned} H_A &= H_{\text{rot}} + H_{\text{inv}} \\ H_{\text{rot}} &= -\frac{\hbar^2}{2}\left[\frac{j_x^2}{I_{xx}(\rho)} + \frac{j_y^2}{I_{yy}(\rho)} + \frac{j_z^2}{I_{zz}(\rho)}\right] \\ H_{\text{inv}} &= -\frac{\hbar^2}{2}\, g(\rho)^{-1/2}\,\frac{\partial}{\partial\rho}\, I_{\rho\rho}^{-1}(\rho)\, g(\rho)^{1/2}\,\frac{\partial}{\partial\rho} + V_{\text{inv}}(\rho) \end{aligned}$$

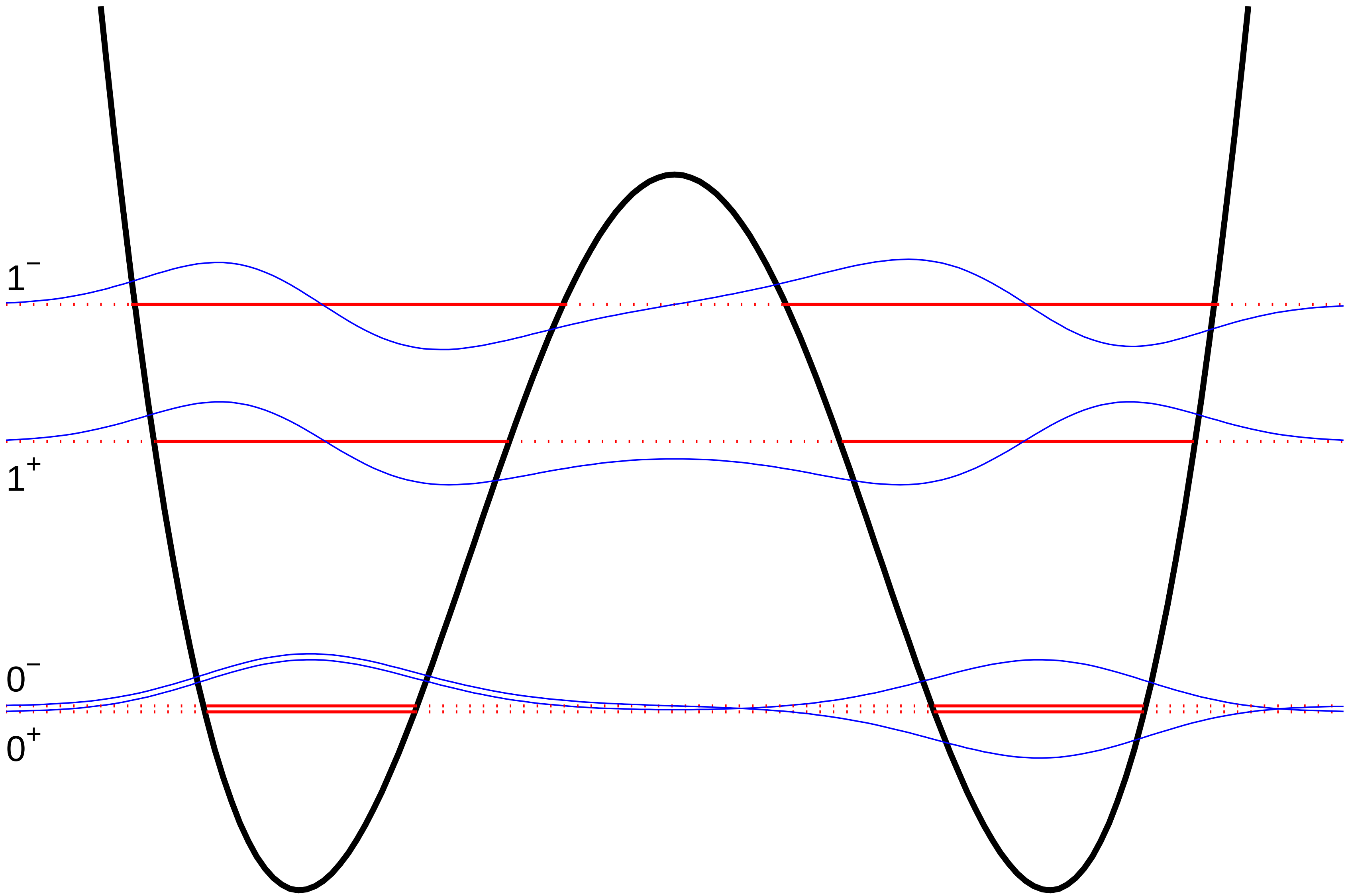
Moments of inertia $\left(\zeta = \frac{m_N}{3m_H + m_N}\right)$

$$\begin{aligned} I_{xx}(\rho) = I_{yy}(\rho) &= 3m_H r_{\text{NH}}^2 \left(\tfrac{1}{2}\sin^2\rho + \zeta\cos^2\rho\right) \\ I_{zz}(\rho) &= 3m_H r_{\text{NH}}^2 \sin^2\rho \\ I_{\rho\rho}(\rho) &= 3m_H r_{\text{NH}}^2 \left(\cos^2\rho + \zeta\sin^2\rho\right) \end{aligned}$$

Metric tensor diagonal, determinant

$$g(\rho) = I_{xx}(\rho) I_{yy}(\rho) I_{zz}(\rho) I_{\rho\rho}(\rho)$$

Potential $V_{\mathrm{inv}}(\rho)$ and vibration-inversion levels $v_2^{\pm}$



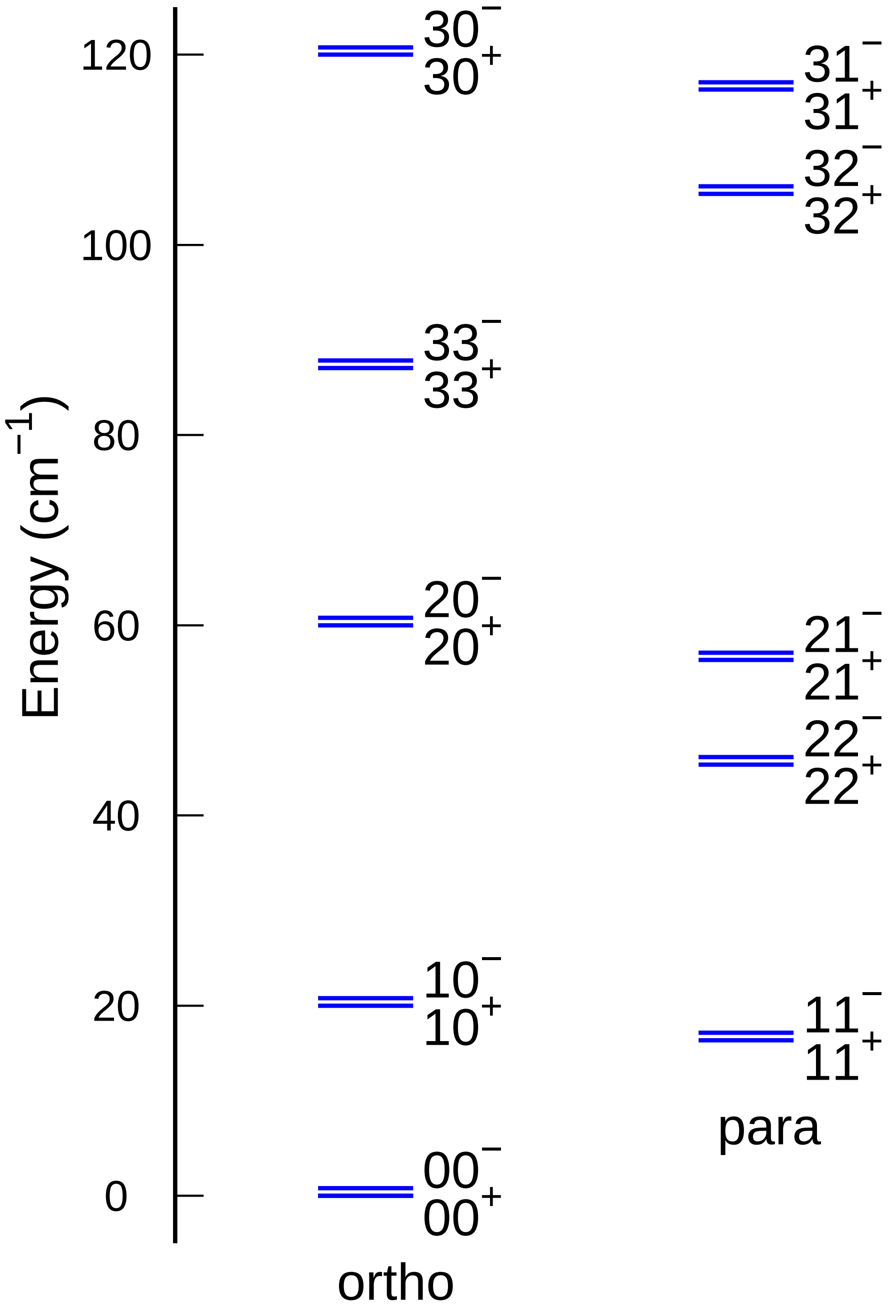
NH$_3$

rotation-

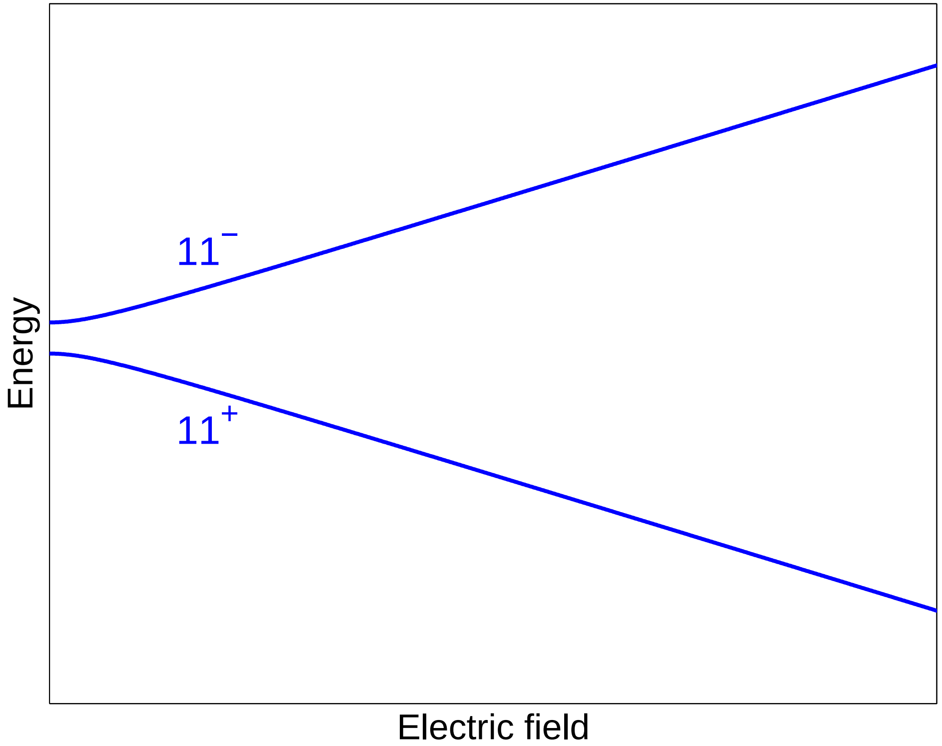
inversion

levels

$(j\,k^{\pm})$



Stark effect in para-NH_3

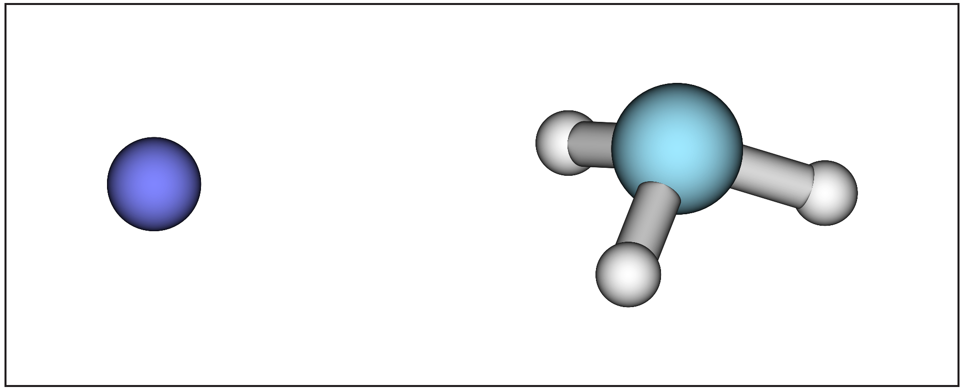


$|\, 11^- \,\rangle$ state (low-field seeking) can be decelerated

$\Rightarrow$ Scattering with velocity-tuned, pure $|\, 11^- \,\rangle$ para-NH_3 or ND_3

NH_3-He potential surface

- Hodges and Wheatley, J. Chem. Phys. **114**, 8836 (2001)
- New potential calculated by CCSD(T)-F12 method in our group



	$R_e\,(a_0)$	$D_e\,(\mathrm{cm}^{-1})$
Hodges	6.13	33.45
ours	6.09	35.08

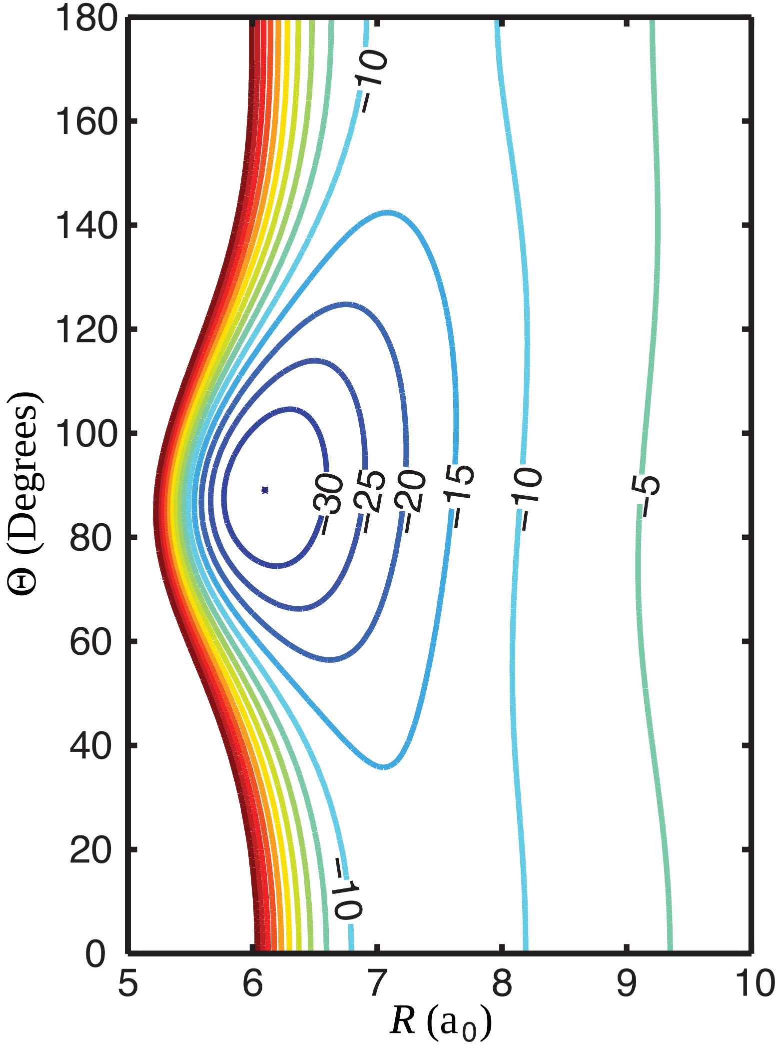
NH_3-He potential

Expanded in spherical harmonics

$$V(R,\rho,\theta,\phi) = \sum_{L,M} v_{LM}(R,\rho) Y_{LM}(\theta,\phi)$$

$v_{LM}(R,\rho)$ expressed analytically in R, ρ

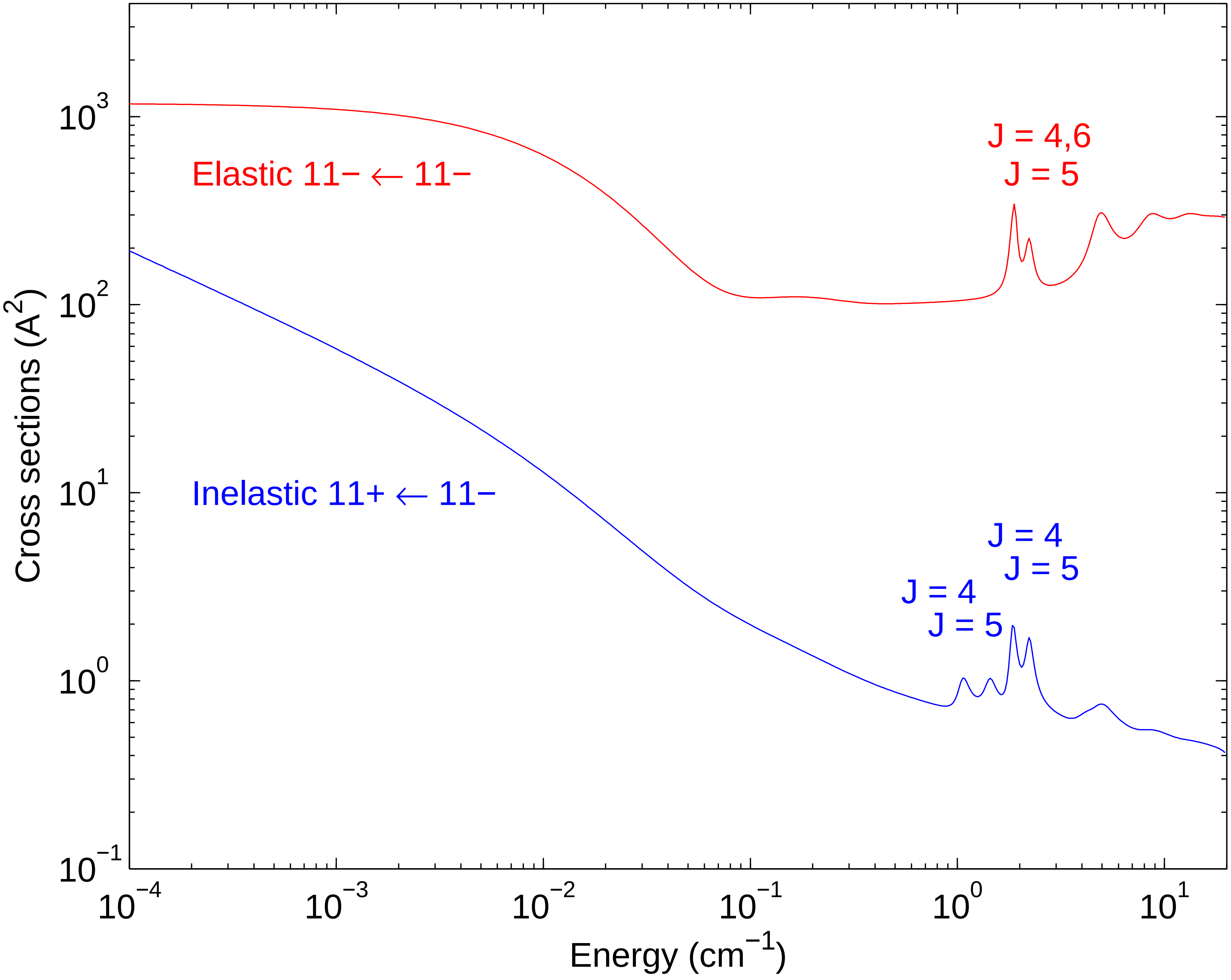
Correct R^{-n} dependence for each L



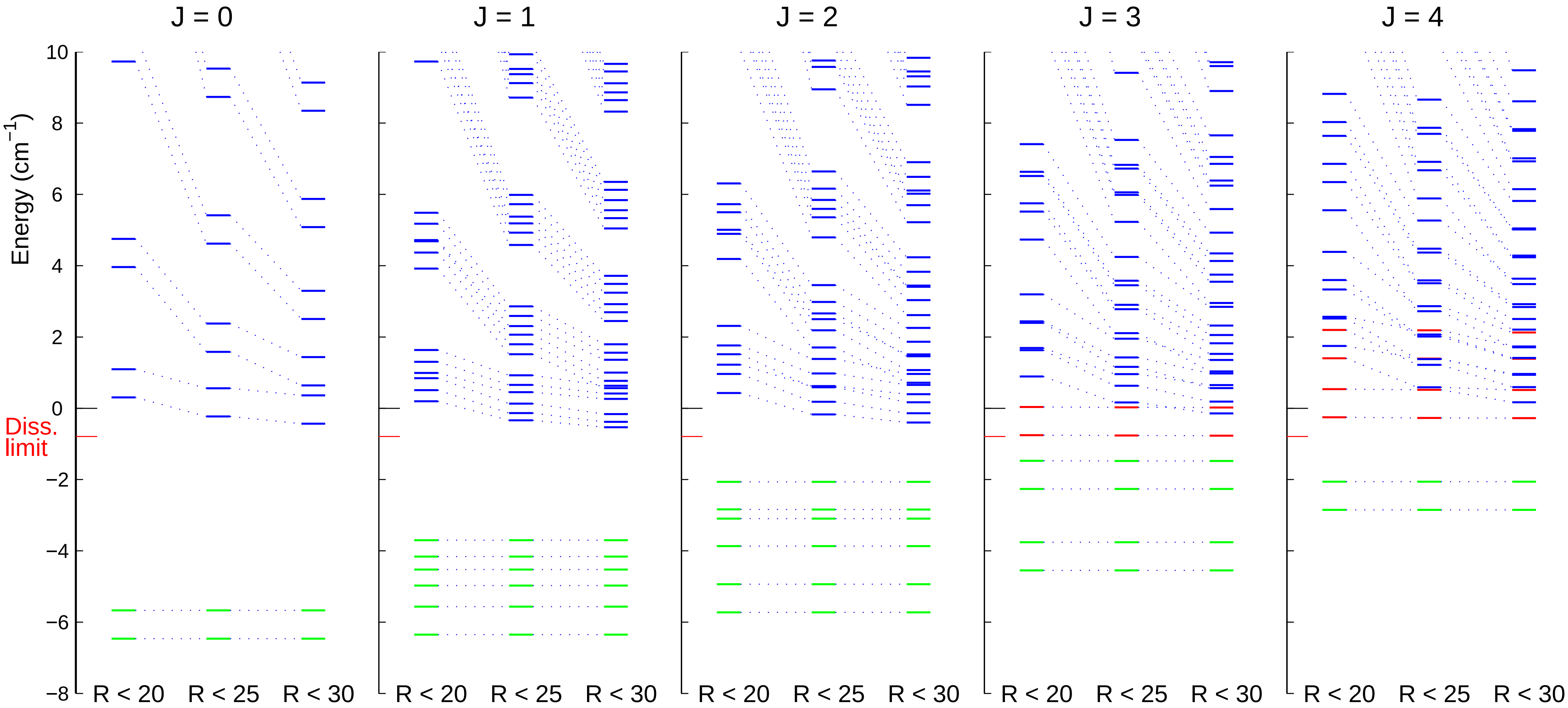
Coupled-channel calculations for NH_3-He

- NH_3 inversion explicitly included (basis $v_2 = 0^\pm, 1^\pm$)
- Apply full $PI(D_{3h})$ symmetry (of collision complex)
  para NH_3-He has E', E'' symmetries, parity ±
- Calculate cross sections $\sigma_{jk^\pm \leftarrow 11^-}$, $\dfrac{d\sigma}{d\Omega}$, phase shifts

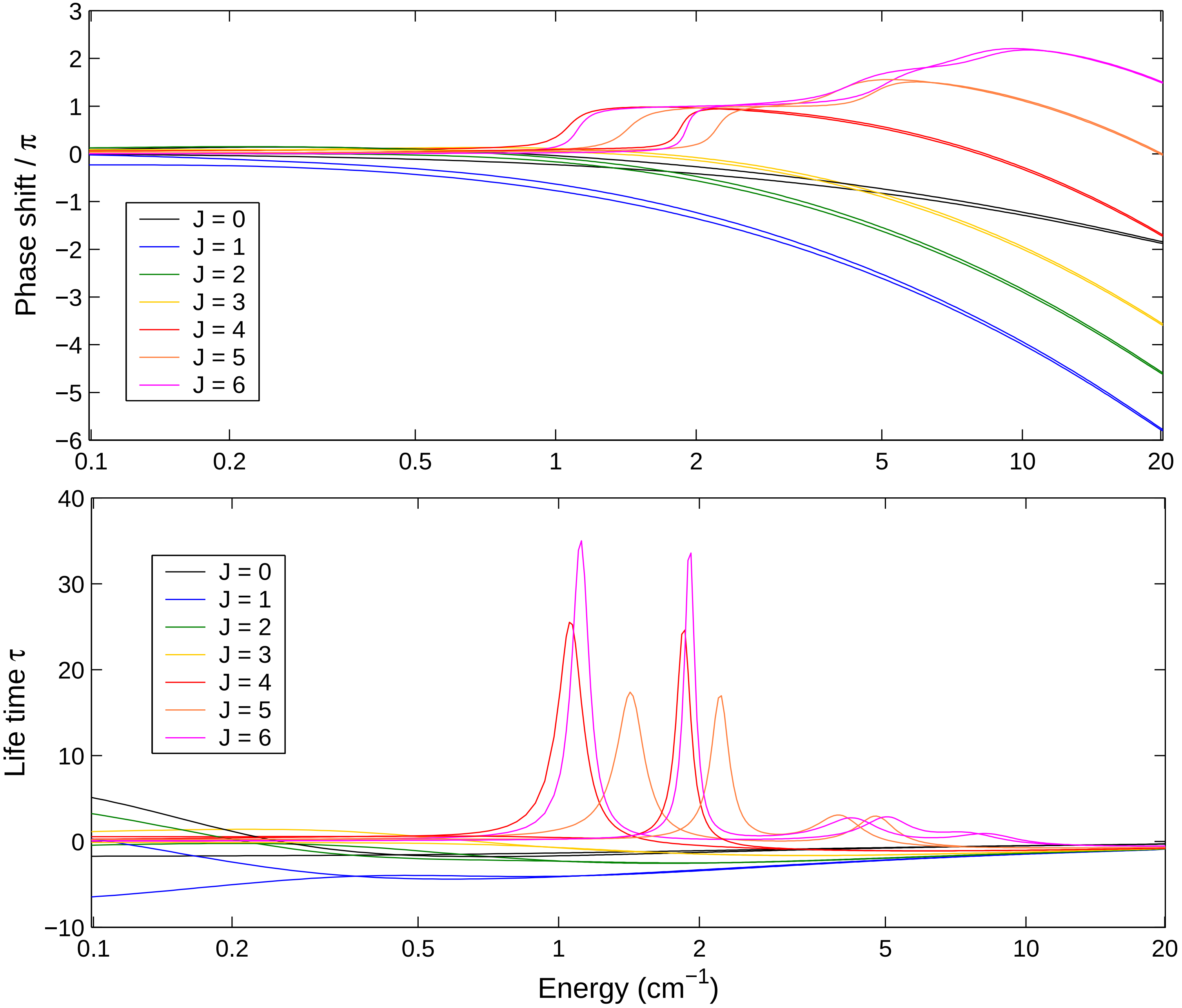
Elastic and inelastic cross sections, orbiting resonances



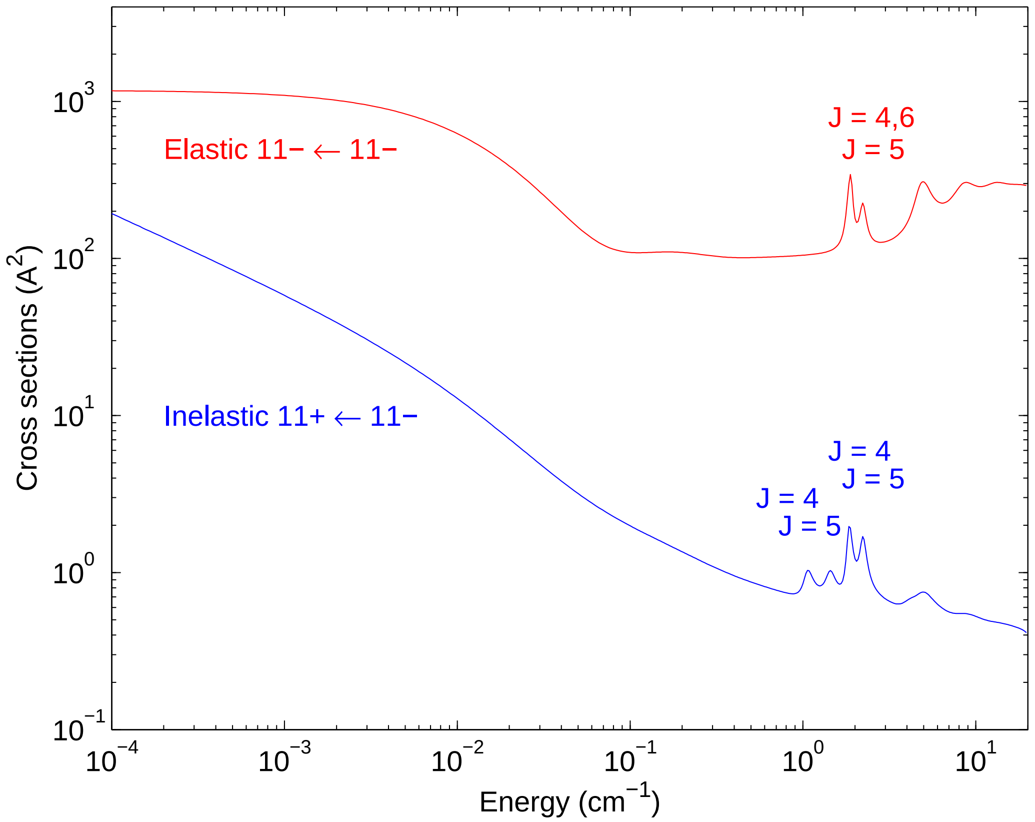
Bound state calculations with $R_{\mathrm{max}} = 20, 25, 30\ a_0$



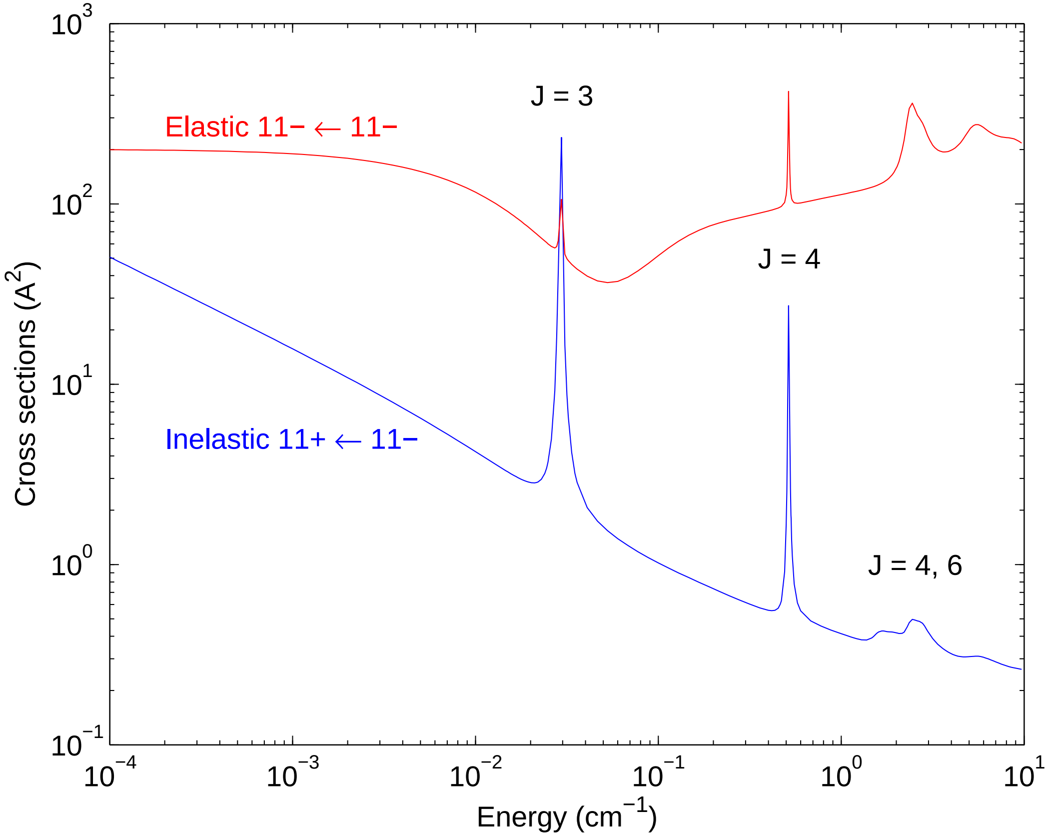
Phase shift, life times



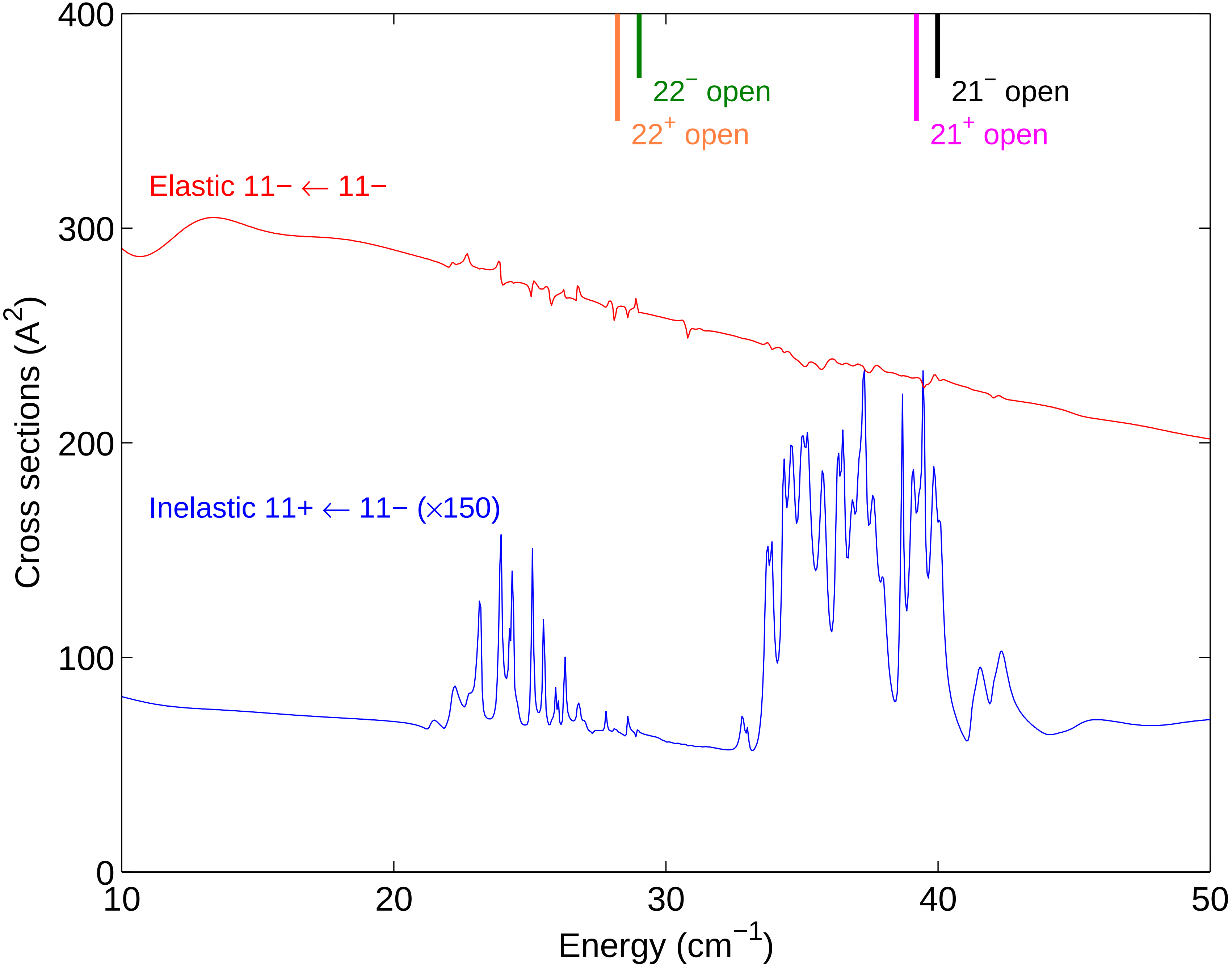
Our potential



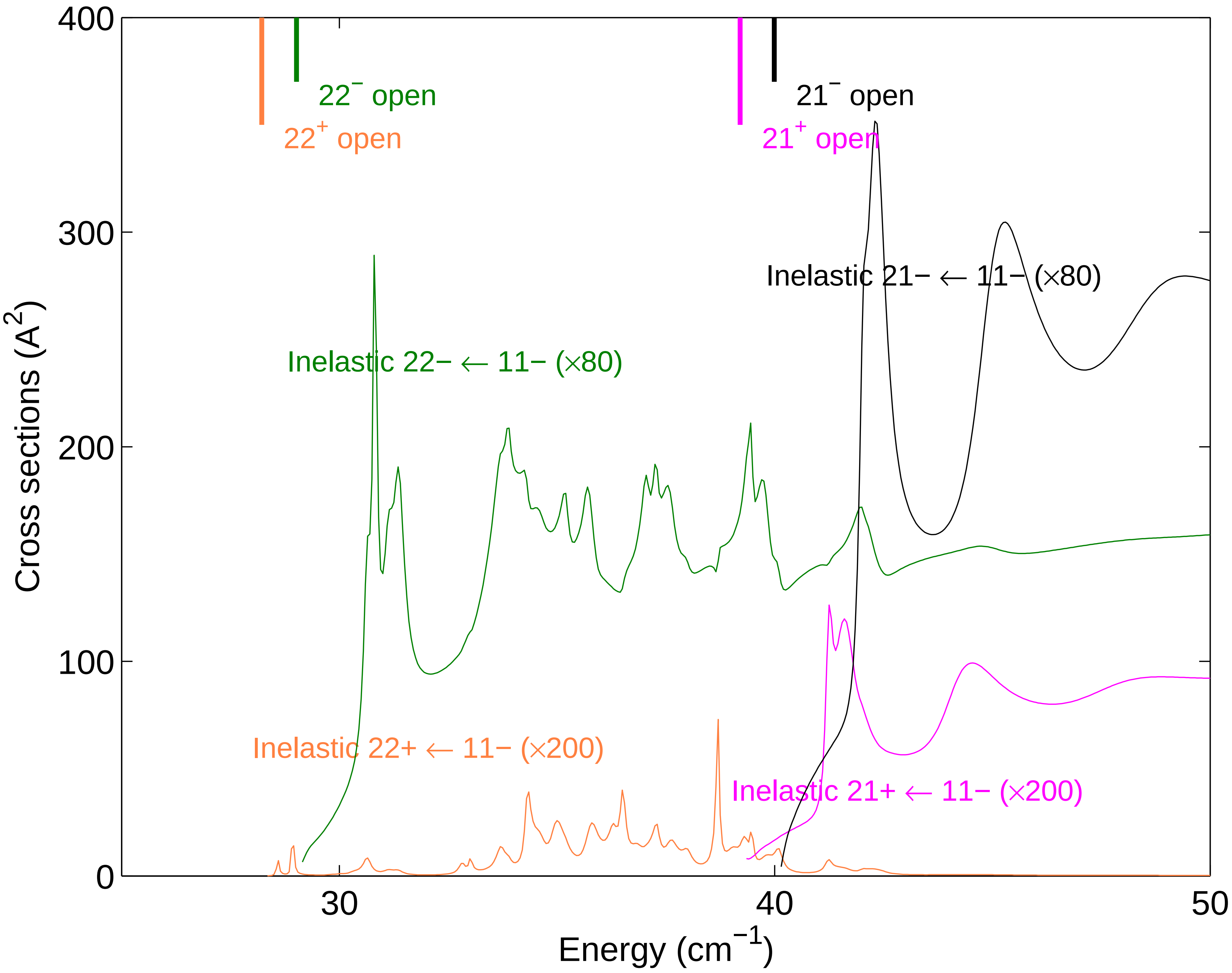
Hodges-Wheatley potential



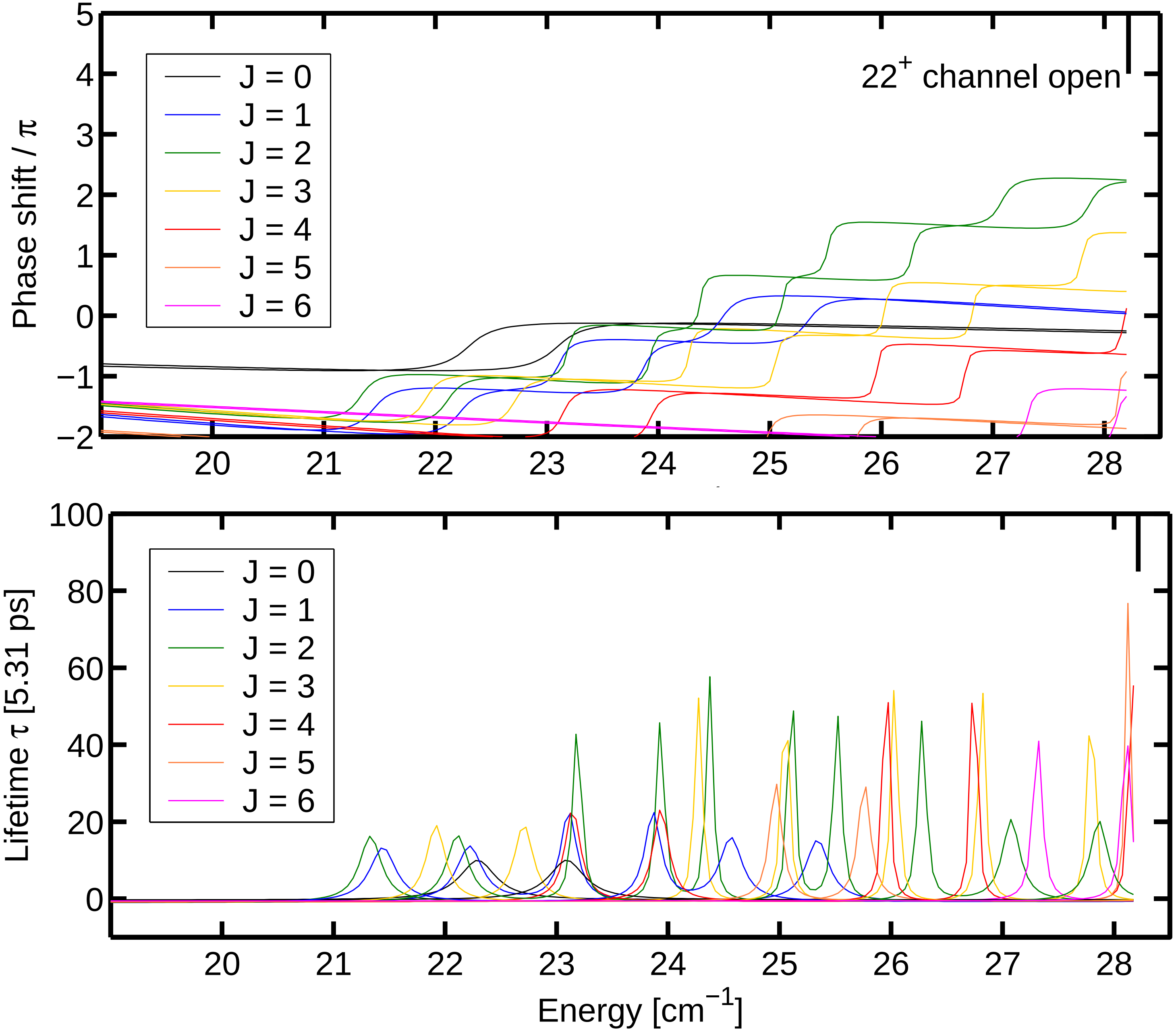
Elastic and inelastic cross sections, Feshbach resonances



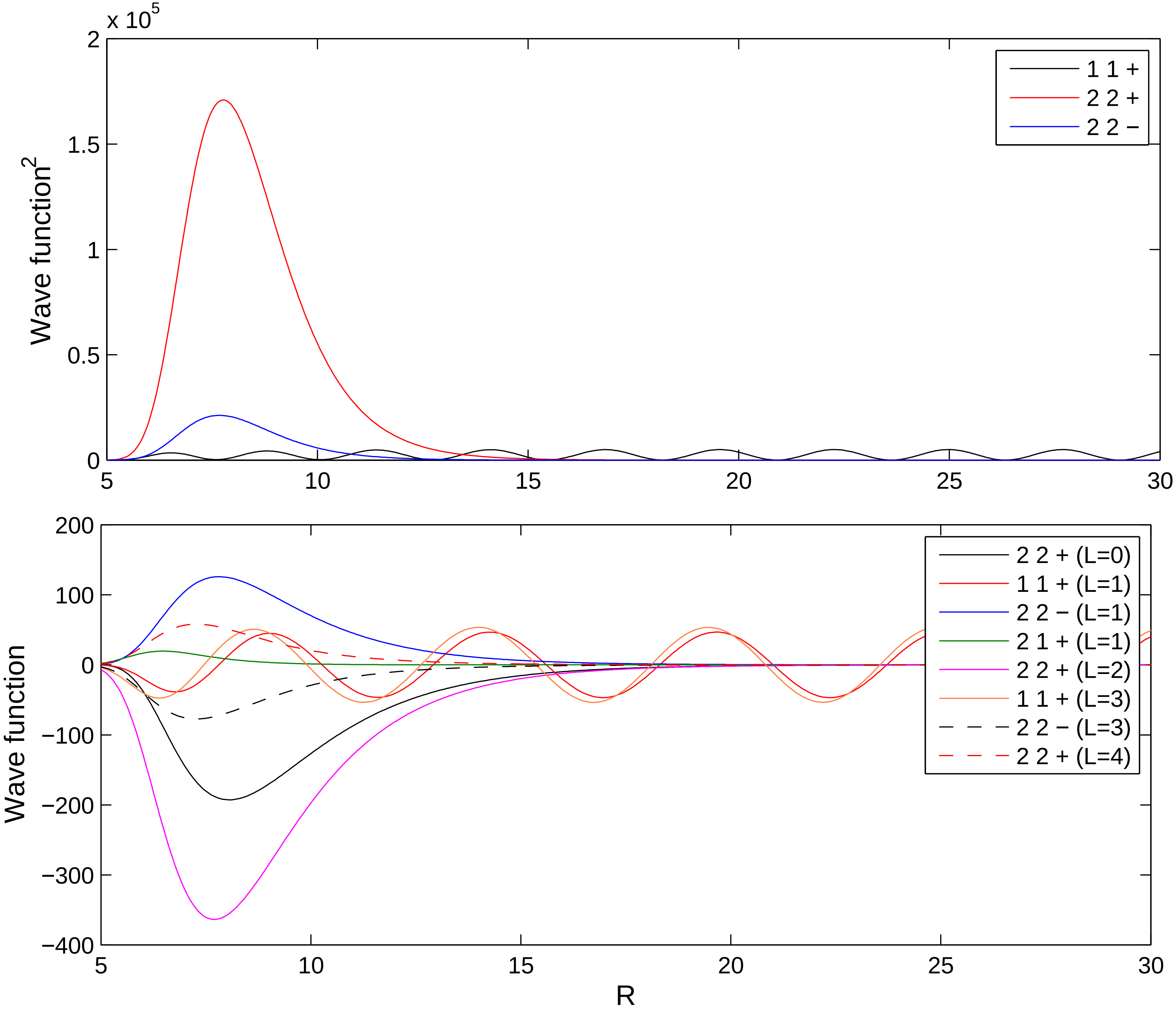
Inelastic cross sections, Feshbach and shape resonances



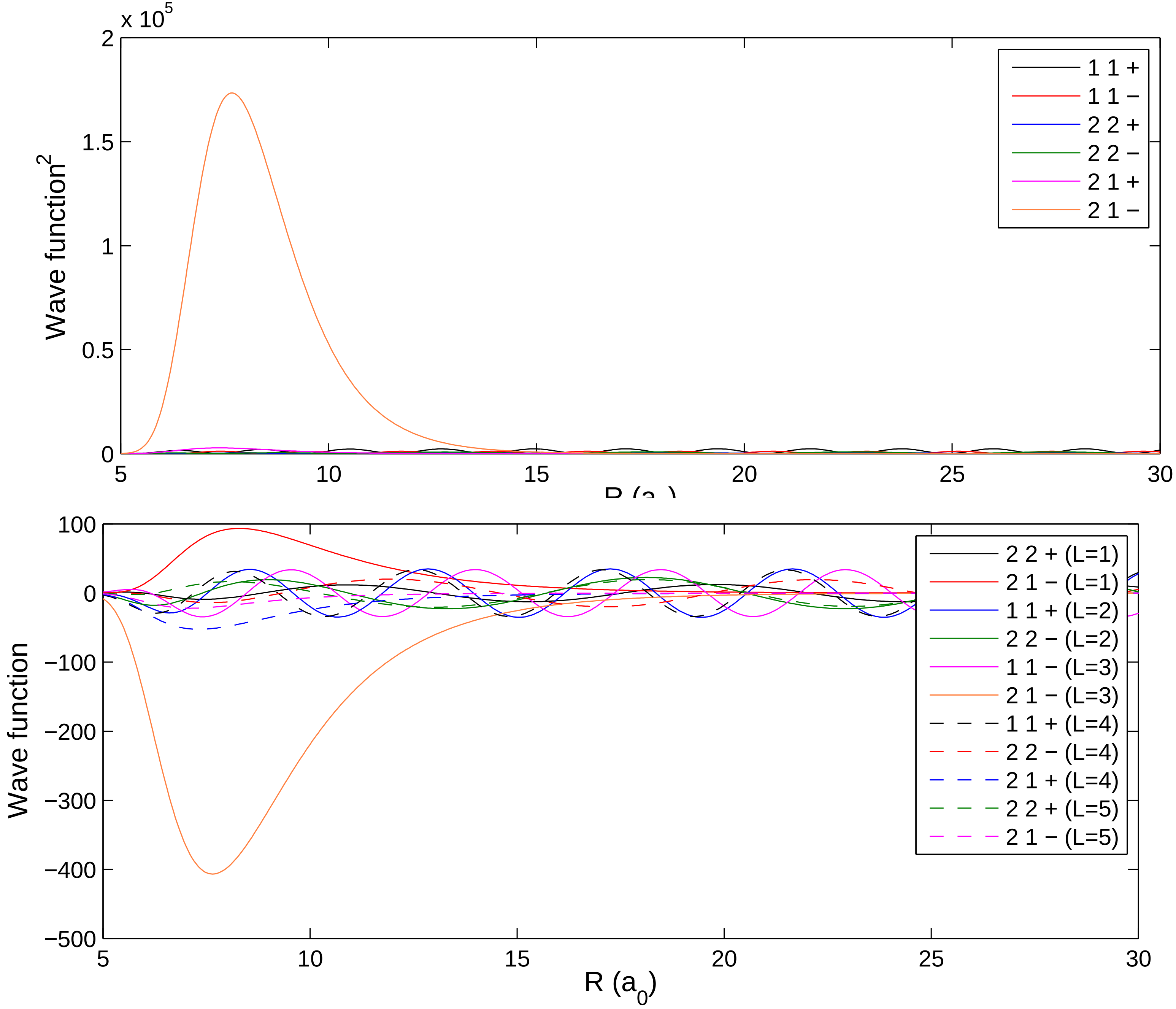
Phase shift, life times



Scattering wave functions at $E = 24.36\ \mathrm{cm}^{-1}$ ($J = 2$, E' symmetry)



Scattering wave functions at $E = 37.28\ \mathrm{cm}^{-1}$ ($J = 3$, E'' symmetry)



Conclusions

- Good agreement between theory and velocity-tuned experiments for OH-X scattering, with X = He, Ne, Ar, Kr, Xe
- Many orbiting and Feshbach resonances found in NH_3-He scattering between 0 and 120 cm^{-1}
- Life times much larger than normal collision times
- Feshbach resonances should be experimentally observable

Acknowledgements

Theory

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