Electric properties of molecules

For a molecule in a uniform electric field$\mathcal{E}$ the Hamiltonian has the form:

$$\hat{H}(\mathcal{E}) = \hat{H} + \mathcal{E}\,\hat{\mu}_x$$

where we assume that the field is directed along the x axis and $\hat{\mu}_x$ is the operator of the x component of the dipole moment ($\mathcal{Z}_n$ is th charge and X_n the x coordinate of nucleus n)

$$\hat{\mu}_x = -\sum_{i=1}^{N} x_i + \sum_n \mathcal{Z}_n\, X_n$$

The energy of the molecule depends then on the field strength $\mathcal{E}$ and can be expanded as a Taylor series in powers of $\mathcal{E}$:

$$E(\mathcal{E}) = E^{(0)} + \mathcal{E}\, E^{(1)} + \mathcal{E}^2\, E^{(2)} + \cdots$$

Using perturbation theory one can show that $E^{(1)}$ is equal to the μ_x component of the permanent dipole moment $\vec{\mu}$ of the molecule:

$$\mu_x = \langle\Psi|\hat{\mu}_x\Psi\rangle$$

The equality $E^{(1)} = \langle\Psi|\hat{\mu}_x\Psi\rangle$ is a special case of the Hellmann-Feynman theorem. This theorem is not valid for approximate methods, e.g, for the MP and the CC methods.

Electric properties of molecules, continued

There are 3 methods of computing the dipole moment (and other first-order properties like, e.g., the quadrupole moment, electron density, forces on nuclei)

- Using the Hellmann-Feynman theorem, i.e., computing $\langle \Psi | \hat{\mu}_x \Psi \rangle$
- Computing the first derivative of $E(\mathcal{E})$ numerically
- Computing the first derivative of $E(\mathcal{E})$ analytically

The most accurate is the third method but we do not always have appropriate computer code. Such codes are available for the SCF, MCSCF, MP2 i CCSD methods.

Second-order energy $E^{(2)}$. that is, the second derivative of $E(\mathcal{E})$, is connected with the polarizability α_{xx} of the molecule:

$$E^{(2)} = -\frac{1}{2}\alpha_{xx}$$

The α_{xx} polarizability is defined through the proportionality of the induced dipole moment $\mu_x(\mathcal{E}) - \mu_x$ to the field strength $\mathcal{E}$ in the limit $\mathcal{E} \to 0$

$$\mu_x(\mathcal{E}) - \mu_x = \alpha_{xx}\,\mathcal{E}$$

The polraizability is a tensor. In general $\alpha_{xx} \neq \alpha_{yy}$ and $\alpha_{xy} \neq 0$ since the field along the x axis can induce a dipole moment in the direction of y axis.

Polarizability - static and dynamic

Standard perturbation theory gives the following expression for α_{xx}

$$\alpha_{xx} = 2 \sum_{k \neq 0} \frac{|\langle \Psi_0 | \hat{\mu}_x \Psi_k \rangle|^2}{E_k - E_0}$$

where E_k and Ψ_k are energies and wave functions of excited states.

Similarly as for the dipole moment we have three methods of computing polarizabilities (and other second-order properties):

- calculations of sum-over excited states
- double numerical differentiation of function $E(\mathcal{E})$
- double analytic differentiation of function $E(\mathcal{E})$

The polarizability discussed thus far is the static polarizability. Very important role in various applications plays also the dynamic polarizability $\alpha_{xx}(\omega)$.

If the electric field oscillates with the frequency ω

$$\mathcal{E}(t) = \mathcal{E}_0 \cos \omega t$$

then he induced dipole moment also oscillates with the frequency ω

$$\mu_x(\mathcal{E}_0, t) - \mu_x = \alpha_{xx}(\omega)\, \mathcal{E}_0 \cos \omega t$$

and the proportionality coefficient $\alpha_{xx}(\omega)$ also depends on the frequency ω.

Dynamic polarizability - excitation energies

Calculating the dipole moment in an oscillating electric field:

$$\mu_x(\mathcal{E}_0, t) = \langle \Psi(\mathcal{E}_0, t) | \hat{\mu}_x \, \Psi(\mathcal{E}_0, t) \rangle$$

requires the knowledge of the time dependence of the wave function. This time evolution of the wave function can be determined from the time-dependent Schrödinger equation:

$$\hat{H}(t)\Psi = i\frac{\partial \Psi}{\partial t}$$

In our case $\hat{H}(t) = \hat{H} + \hat{\mu}_x \, \mathcal{E}_0 \cos \omega t$.

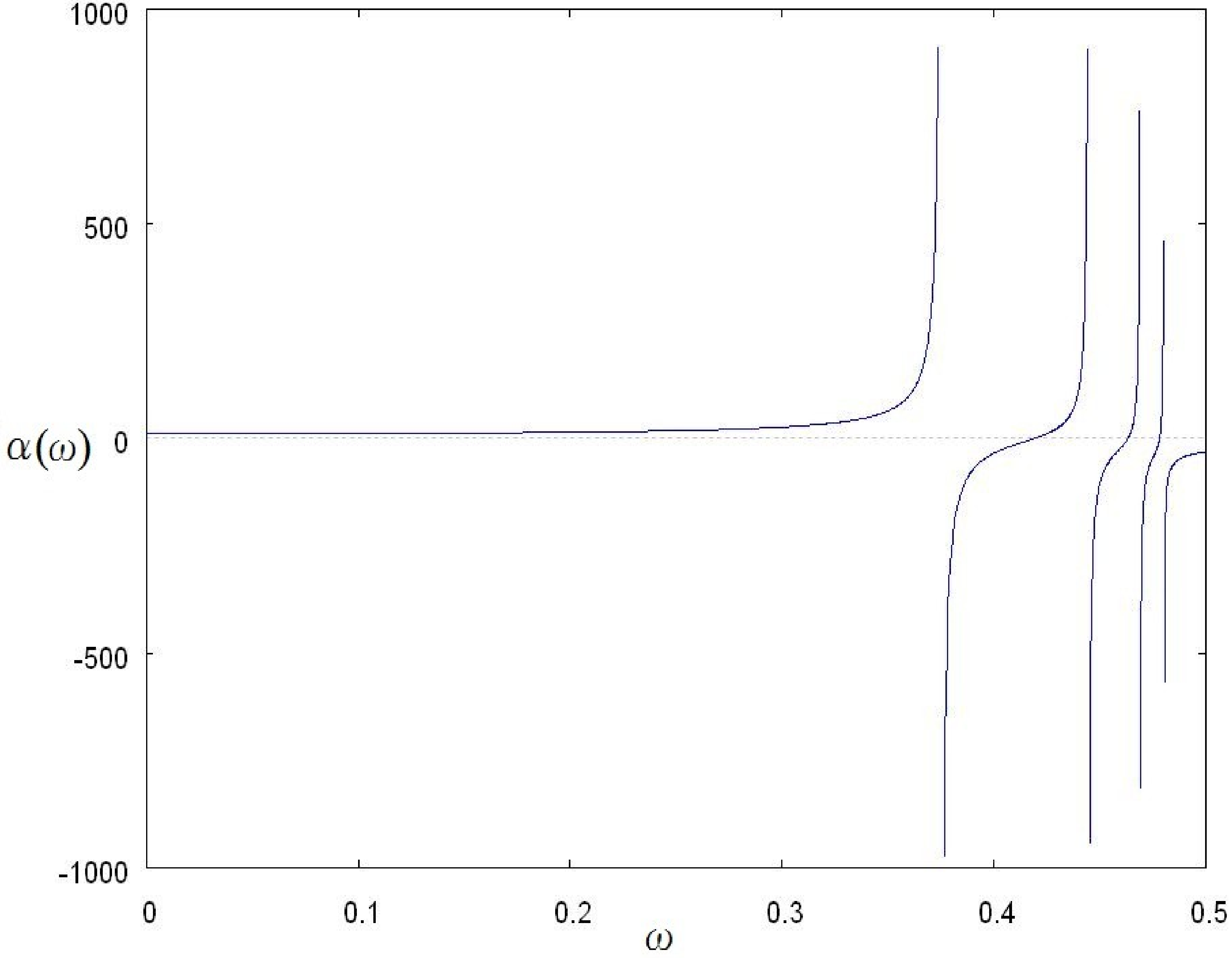
Applying the perturbation theory to the time-dependent Schrödinger equation we obtain the following expression for $\alpha_{xx}(\omega)$:

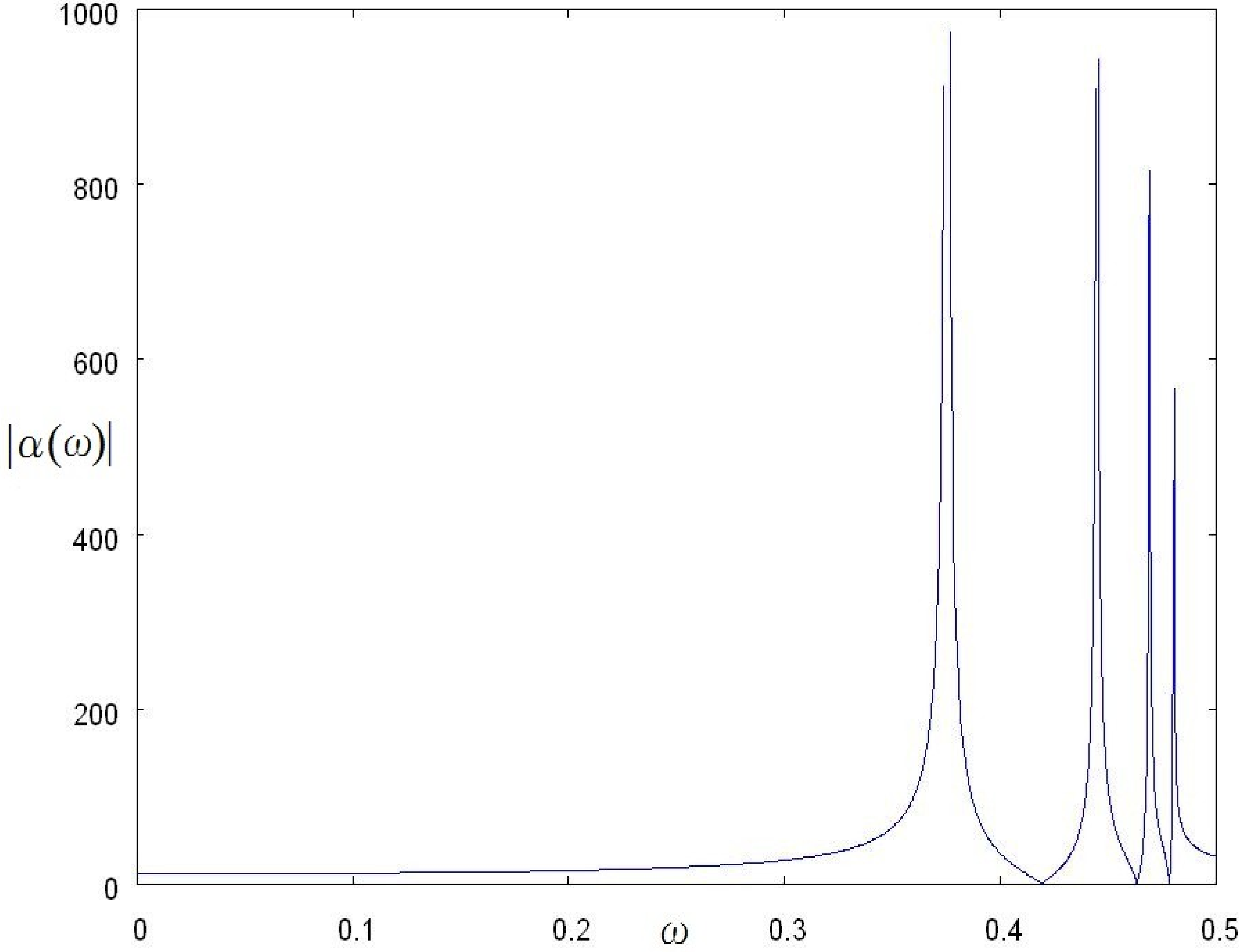
$$\alpha_{xx}(\omega) = \sum_{k \neq 0} \left(\frac{|\langle \Psi_0 | \hat{\mu}_x \Psi_k \rangle|^2}{\omega_{k0} + \omega} + \frac{|\langle \Psi_0 | \hat{\mu}_x \Psi_k \rangle|^2}{\omega_{k0} - \omega}\right)$$

where $\omega_{k0} = E_k - E_0$ excitation energies of the system. This equation shows that $\alpha_{xx}(\omega)$ has simple poles for ω's coinciding with the excitation energies of a molecule. The residues of these poles

$$\lim_{\omega \to \omega_{k0}} (\omega_{k0} - \omega)\alpha_{xx}(\omega) = |\langle \Psi | \hat{\mu}_x \Psi_k \rangle|^2$$

determine the probabilities (intensities) of dipole transitions in spectroscopy.


1000
500
0
-500
-1000
$\alpha(\omega)$
0
0.1
0.2
0.3
0.4
0.5
ω


1000
800
600
400
200
0
$|\alpha(\omega)|$
0
0.1
0.2
ω
0.3
0.4
0.5

Dynamic polarizability - excitation energies, continued

Dynamic polarizability contains information about:

- excitation energies
- transition probabilities (the dipole ones)
- light scattering intensity
- refraction coefficient
- interaction energies (of the dispersion type)

Dynamic polarizability, and therefore the excitation energies can be computed using the following methods:

- Time-dependent Hartree-Fock theory (TD-HF)
- Time-dependent coupled-cluster theory (TD-CC)
- Time-dependent density functional theory (TD-DFT)

With respect of the increasing accuracy these methods can be ordered in the following way (from least accurate to the more accurate)

CIS < TD-HF < TD-DFT < TD-CCSD < MRCISD < TD-CCSDT

Time-dependent Hartree-Fock Theory, TD-HF

- In the TD-HF method the wave function $\Psi(\mathcal{E}_0, t)$ is a Slater determinant built from orbitals $\phi_k(\mathcal{E}_0, t)$ depending on time.
- Orbitals $\phi_k(\mathcal{E}_0, t)$ are determined using the time-dependent variational principle (Frenkel's variational principle).
- Poles of the dynamic polarizability (excitation energies) are obtained by diagonalizing the Hessian matrix of the usual time-independent Hartree-Fock theory
- TD-HF excitation energies are real only when the Hessian matrix has positive eigenvalues
- Excitation energies (and dynamic polarizabilities) of the TD-HF method can also be derived using the so-called random phase approximation (RPA) theory, which is time-independent. Note, there exists many variants of the RPA theory. Only one of them is equivalent to the TD-HF method.
- For states with a nonzero spin one can use restricted (TD-ROHF) or unrestricted (TD-UHF) time-dependent Hartree-Fock theory

Time-dependent coupled cluster theory, TD-CCSD

- **In the TD-CCSD theory the cluster operator $\hat{T}$ depends on time t, $\hat{T}(t) = \hat{T}_1(t) + \hat{T}_2(t)$. The wave function is assumed in the form:**

$$\Psi(t) = N(t)\, e^{\hat{T}(t)}\, \Phi_0$$

- **The normalization constant $N(t)$ and the coefficients determining the $\hat{T}_1(t)$ and $\hat{T}_2(t)$ operators are found by substituting $\Psi(t)$ into the time-dependent Schrödinger equation and projecting on all singly-and doubly excited determinants (Galerkin-Pietrov method).**
- **Excitation energies are obtained by diagonalizing the matrix of the operator**

$$e^{-\hat{T}}\hat{H}e^{\hat{T}}$$

in the basis of singly-and doubly excited determinants .

- **The TD-CCSD method gives the same excitation energies as the so-called equation of motion method (EOM-CCSD). The name EOM-CCSD is now more frequently used than TD-CCSD.**
- **The variant EOM-CCSDT has been recently developed. This is the most accurate method of computing excitation energies of molecules.**
- **The TD-CC method was discovered by quantum chemists. Somewhat later the same method was developed by nuclear physicists.**

Intermolecular interactions

The interaction energy of molecule A and B is defined as:

$$E_{\text{int}} = E(AB) - E(A) - E(B)$$

where $E(AB)$, $E(A)$ i $E(B)$ are the electronic energies (for fixed nuclear positions)) of the dimer AB and the monomers A and B, respectively. The geometries of molecules A i B are assumed to be exactly the same as in the dimer AB.

The interaction energy E_{int} depends on:

- **the distance R between molecules A i B**
- **the mutual orientation of molecules l A i B**
- **electronic quantum states of molecules l A i B**
- **internal geometry of molecules A i B**

There exists two general method of computing the interaction energy:

– The supermolecular method

– The perturbation method - Symmetry-Adapted Perturbation Theory (SAPT)

Intermolecular interactions. The supermolecular method

In the supermolecular method we compute approximate electronic energies $\widetilde{E}(AB)$, $\widetilde{E}(A)$ i $\widetilde{E}(B)$ for the dimer AB and for the monomers A and B employing an approximate method X (e.g., X= HF, CCSD, DFT) and we carry out the subtraction

$$\widetilde{E}_{\rm int} = \widetilde{E}(AB) - \widetilde{E}(A) - \widetilde{E}(B)$$

This method relies on a cancellation of errors in taking the difference.

The necessary conditions for this cancellations are

– size consistency of method X)
– application of exactly the same basis set for the dimer AB, and for each of the monomers A and B

The error arising when the basis A or basis B forms a subset of basis AB is called the basis set superposition error (BSSE).

This error, always negative, can be significant for small basis sets and should always be eliminated. The procedure of its elimination - the so-called Counter-Poise (CP) correction was proposed by Boys and Bernardi.

The main advantage of the supermolecular method is its simplicity and universality. Disadvantages: error cancellation may not occur, missing insight into the nature of the interaction (its dependence on monomer properties), extra cost of eliminating BSSE.

Intermolecular interactions. The perturbation method - SAPT

Using the symmetry-adapted perturbation theory one can show (unless the intermolecular distances are too small) that the interaction energy is represented in a good approximation as the sum

– Electrostatic interaction energy
– Induction interaction energy
– Dispersion interaction energy
– Exchange interaction energy

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{ind}} + E_{\text{disp}} + E_{\text{exch}}$$

The electrostatic interaction energy represents the usual Coulomb interaction of electric charge distribution in monomers :

$$E_{\text{elst}} = \int\int \frac{\rho^A(\vec{r}_1)\rho^B(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|} d\tau_1 d\tau_2 \quad \text{where} \quad \rho^X(\vec{r}) = \sum_{n\in X} \rho_n(\vec{r}) - \rho^X_{\text{el}}(\vec{r})$$

$\rho^X_{\text{el}}(\vec{r})$ is the distribution of the electric charge of electrons, $\int \rho^X_{\text{el}}(\vec{r}) d\tau = N_X$

$\rho_n(\vec{r})$ is the distribution of the positive charge of nucleus n, $\int \rho_n(\vec{r}) d\tau = Z_n$

One can assume that $\rho_n(\vec{r})$ is the Dirac delta $\delta(\vec{r} - \vec{R}_n)$ localized on nucleus n

Electrostatic interaction energy, continued

At large distances R the electrostatic energy E_{elst} behaves as :

$$E_{\mathrm{elst}} \sim \frac{1}{R^{l_A+l_B+1}}$$

where, we assume that the 2^{l_X}-pole moment is the lowest non-vanishing multipole moment of molecule X

The 2^{l_X}-pole moment M_l^m of molecule is defined as :

$$M_l^m = \langle \Psi | \hat{M}_l^m \Psi \rangle$$

where $\hat{M}_l^m$ is the operator of the mth component of the 2^l-pole moment:

$$\hat{M}_l^m = \sqrt{\frac{4\pi}{2l+1}} \sum_i q_i \, r_i^l \, Y_l^m(\theta_i, \phi_i)$$

(the summation goes here over all charges q_i in the molecule).

If the molecules have a dipole moments $\vec{\mu}^A$ and $\vec{\mu}^B$ (l_A=l_B=1) then the dipole-dipole interaction of the form

$$E_{\mathrm{elst}} = \frac{1}{R^3}[\vec{\mu}^A \cdot \vec{\mu}^B - 3(\vec{\mu}^A \cdot \vec{n})(\vec{\mu}^B \cdot \vec{n})],$$

where $\vec{n} = \vec{R}/R$, dominates at large R.

Induction interaction

The energy of this interaction depends on the static polarizability α_X, X=A,B of molecules. It is the result of the interaction of a multipole on A with a dipole induced on molecule B by the electric field of molecule A.

Since the electric field of the 2^l-pole M_l^m decreases with the distance as $1/R^{l+2}$ therefore the induced dipole on B is of the order of

$$\mu_B \sim \frac{\alpha_B \, M_l^m}{R^{l+2}}$$

Interaction of this induced dipole μ_B with the inducing 2^l-pole is hence of the following order:

$$E_{\mathrm{ind}} \sim \frac{\mu_B \, M_l^m}{R^{l+1+1}} = \frac{\alpha_B \, (M_l^m)^2}{R^{2l+4}}$$

If M_l^m is the dipole, l=1, the induction energy decreases asymptotically as $1/R^6$:

$$E_{\mathrm{ind}} \sim \frac{\alpha_B \, \mu_A^2}{R^6}$$

At smaller distances higher multipoles give a significant contribution to the induction energy. At short range the induction leads to a strongly attractive contribution resulting from overpolarization (polarization catastrophe).

Dispersion interaction

This interaction is a result of the induction-type interaction of instantaneous (momentary) multipoles appearing due to the quantum fluctuations of atomic or molecular charge densities.

It occurs also between atoms, which do not possess permanent multipole moments.

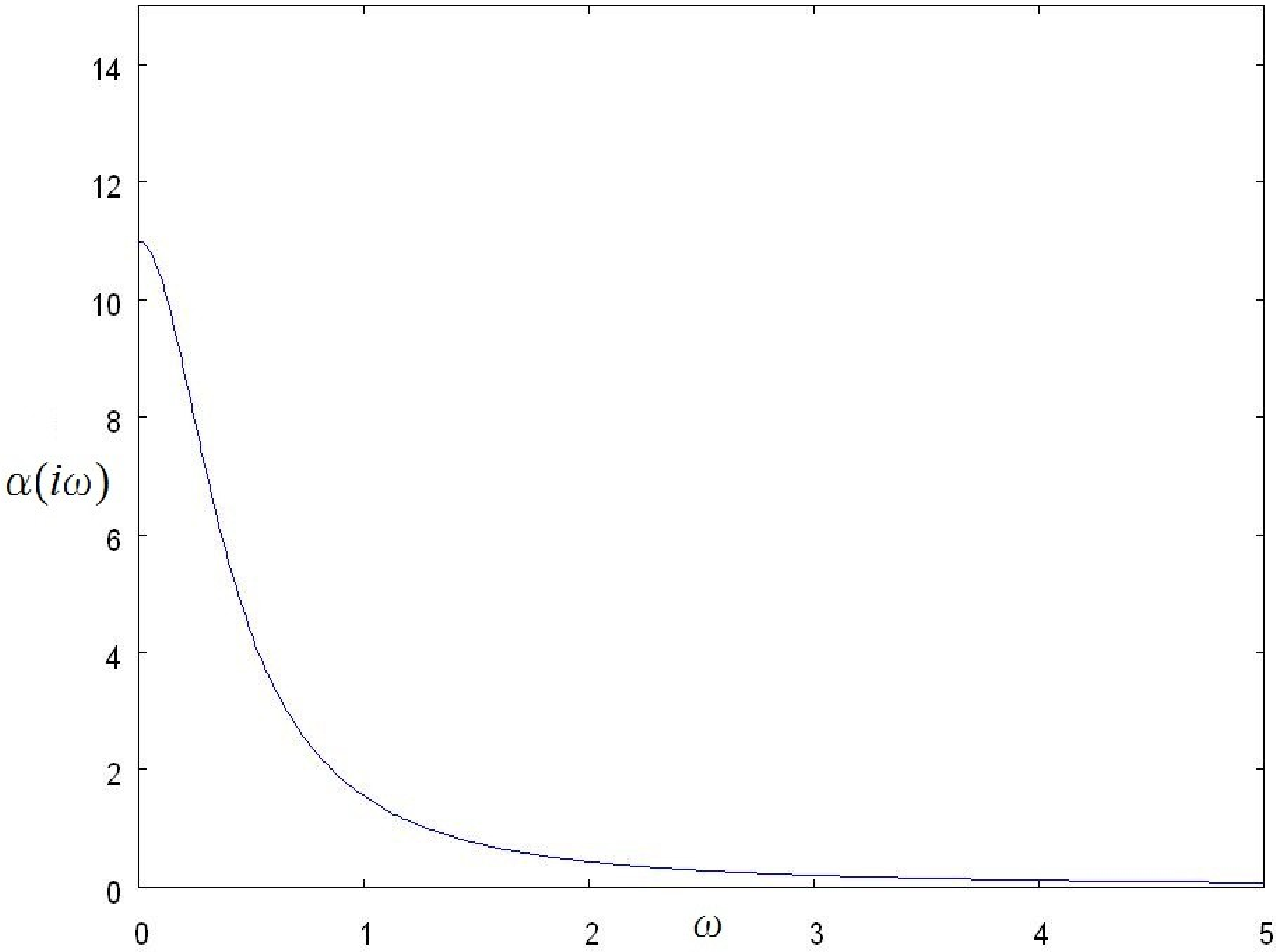
Since fluctuations always generate momentary dipoles this interaction decreases always as $C_6\, R^{-6}$.

One can show, that for large R the dispersion interaction is determined by the dynamic polarizabilies at imaginary frequencies $i\omega$:

$$C_6 = -\frac{3}{\pi}\int_0^\infty \alpha_A(i\omega)\,\alpha_B(i\omega)d\omega$$

where

$$\alpha_X(i\omega) = \sum_{k\neq 0}(\frac{|\langle\Psi_0|\hat{\mu}_x\Psi_k\rangle|^2}{\omega_{k0}+i\omega}+\frac{|\langle\Psi_0|\hat{\mu}_x\Psi_k\rangle|^2}{\omega_{k0}-i\omega}) = 2\sum_{k\neq 0}\frac{\omega_{k0}\,|\langle\Psi_0|\hat{\mu}_x\Psi_k\rangle|^2}{\omega_{k0}^2+\omega^2}$$



14
12
10
8
$\alpha(i\omega)$
6
4
2
0
0
1
2
ω
3
4
5

Exchange interaction

This interaction is a result of the Pauli principle and the (resonance) tunneling of electrons between interacting atoms or molecules.

It has the following properties:

- **It has a short range — vanishes exponentially with the distance R,**

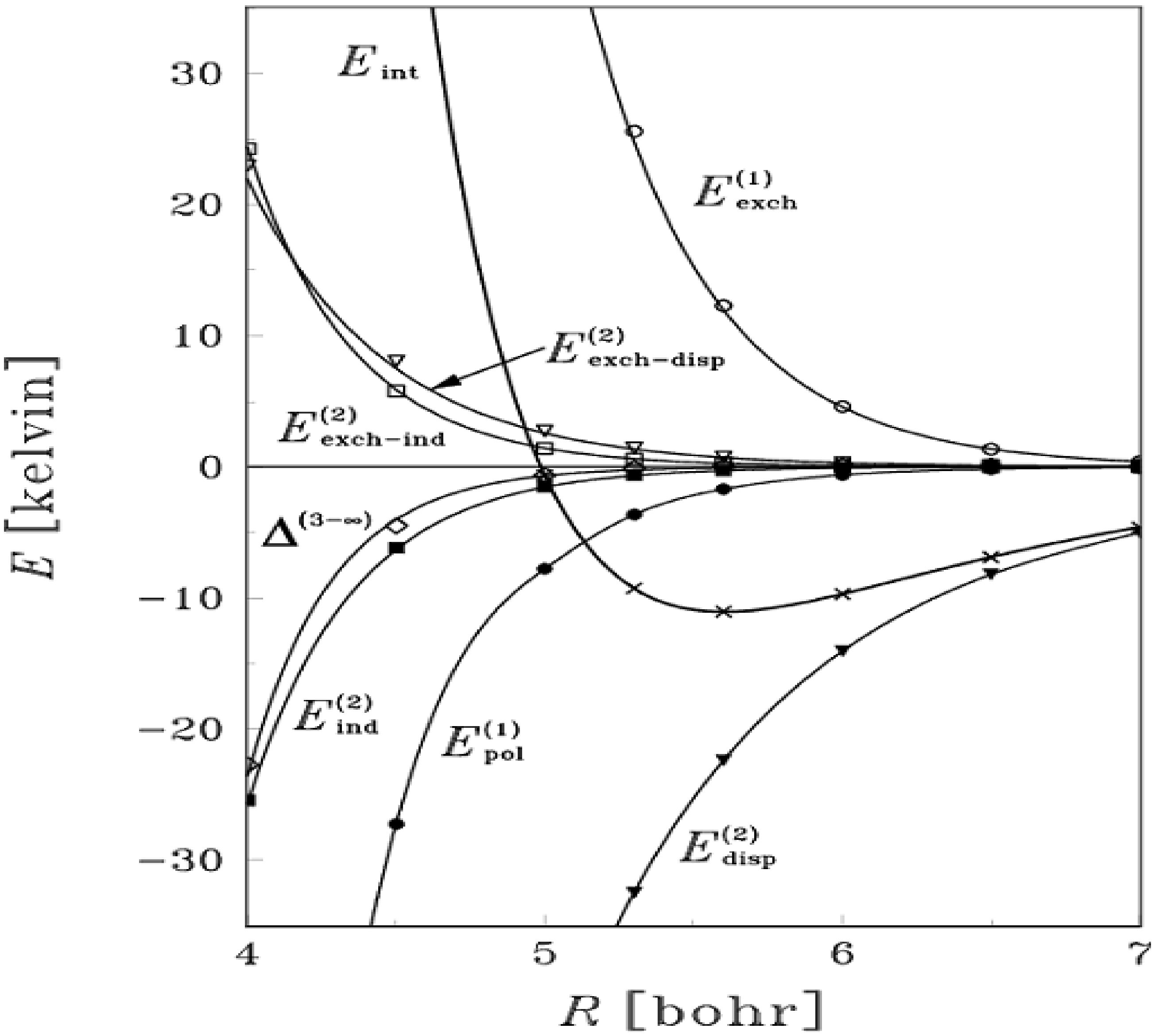
$$E_{\rm exch} \sim R^{\gamma}\, e^{-\alpha R}$$

- **For small R it is proportional to the overlap of the wave functions of the interacting molecules A and B**
- **For the interaction of closed-shall systems it is always repulsive. It represents the main repulsive component of the interaction energy**
- **We know, that for two hydrogen atoms $E_{\rm exch}$ vanishes at large R according to the formula**

$$E_{\rm exch} = \pm\, 0.818\, R^{5/2}\, e^{-2R}$$

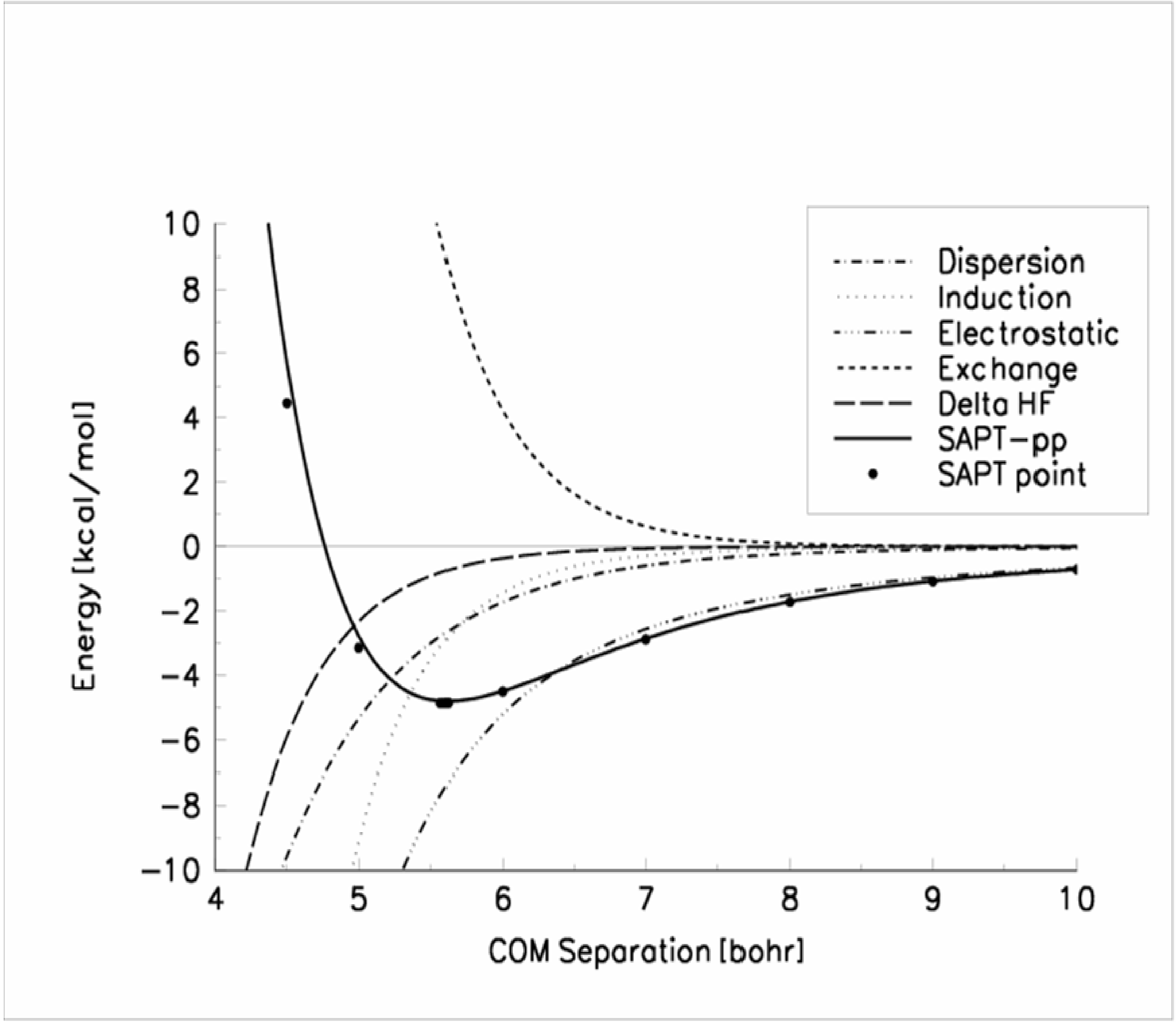
  where the $+$ is for the triplet and the $-$ for the singlet
- **It is very difficult to compute accurately, especially at large R**

Interaction energy components for the helium dimer



The electrostatic interaction energy $E^{(1)}_{\text{elst}}$ is denoted here by $E^{(1)}_{\text{pol}}$. The symbols $E^{(2)}_{\text{exch-ind}}$ and $E^{(1)}_{\text{exch-disp}}$ denote (very small) exchange-induction and exchange dispersion components

Interaction energy components for the water dimer



Resonance interaction

This interaction occurs between identical atoms or molecule when they are in different quantum states.

At large R the wave function for the dimer AB is then not a product $\Psi_0^A\,\Psi_n^B$ of the monomer wave functions but must be a superposition of two resonance structures

$$\Psi^{AB} = \frac{1}{\sqrt{2}}(\Psi_0^A\,\Psi_n^B \pm \Psi_n^A\,\Psi_0^B)$$

This is a long-range interaction – decaying withe the distance as $\sim 1/R^{2l+1}$

$$E_{\mathrm{res}} \sim \frac{|\langle\Psi_0^A|\hat{M}_l^m\Psi_n^A\rangle|^2}{R^{2l+1}}$$

where l is the smallest value of l for which the matrix element $\langle\Psi_0^A|\hat{M}_l^m\Psi_n^A\rangle$ does not vanish. E_{res} is inversely proportional to the life-time of the excited state.

If the dipole transition, $l{=}1$, is allowed, that is if $\langle\Psi_0^A|\hat{M}_1^m\Psi_n^A\rangle \neq 0$, the resonance interaction vanishes as $\sim 1/R^3$.

Casimir interaction (retardation)

This is dispersion-type interaction, resulting from the finite speed c of the propagation of electromagnetic interactions. This is, thus, a relativistic effect. This interaction occurs due to the exchange of (virtual) photons between interacting systems

For small distances this interaction behaves as C_4/R^4, where the constant C_4 is proportional to $1/c^2$

For vary large distances, $R > 100$ bohr, the relativistic contributions completely cancels the usual dispersion (London) interaction and the remaining interaction energy vanishes as $\sim 1/R^7$, and in particular as

$$E_{\text{int}} \sim \frac{c\,\alpha_A(0)\,\alpha_B(0)}{R^7}$$

The weakening of the interaction by one power of R is a result of the fact, that the induced dipole interacts with some delay with the inducing one, so the latter changes its orientation during the time of the photon flight.

This interaction was discovered in 1940 the Netherlands (Vervey i Overbeek) by investigating the properties of colloids. It was theoretically explained by Hendrik Casimir in 1948 as an effect of the finite speed of light.