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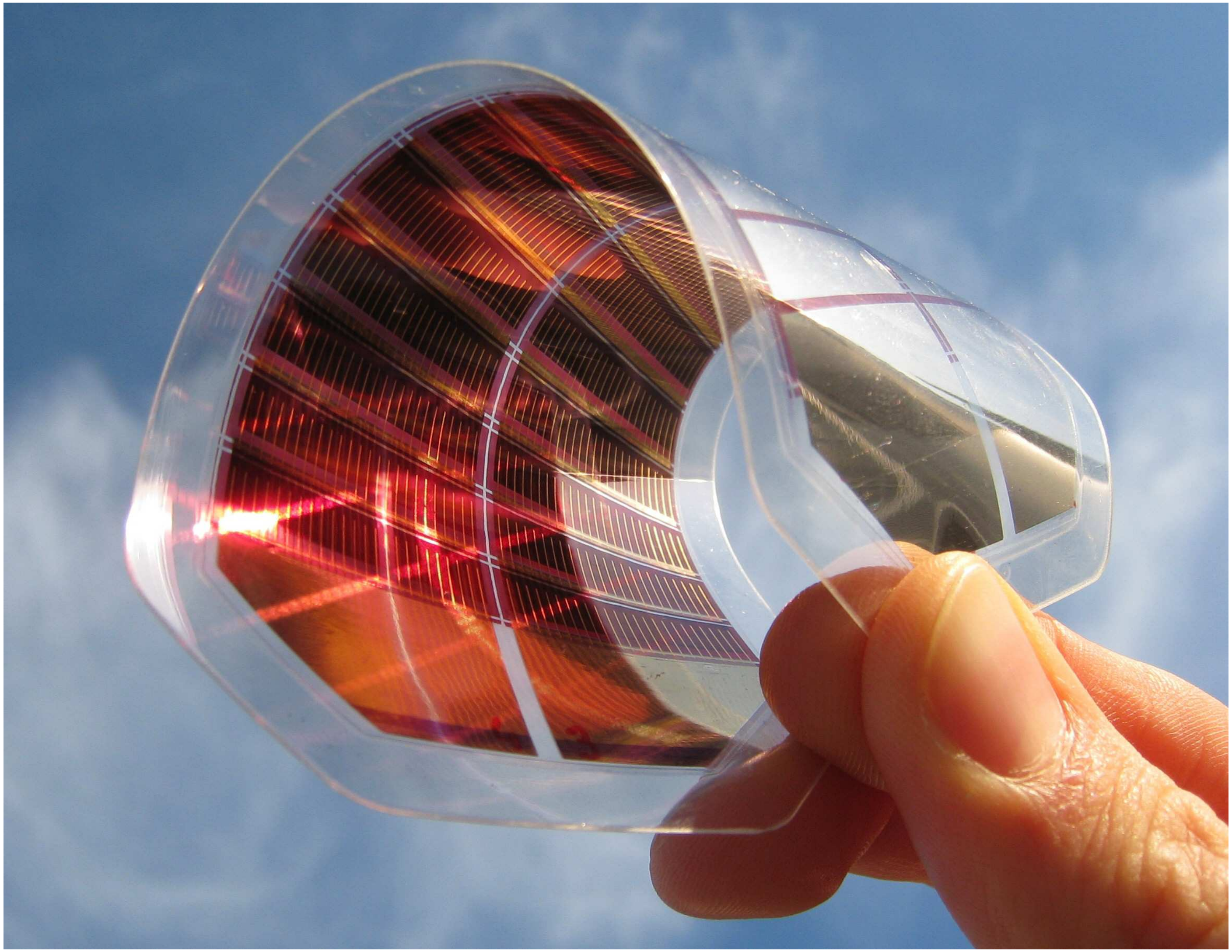
Simulating charge transfer in (organic) solar cells

Harald Oberhofer

July 24, 2013

Organic solar cells



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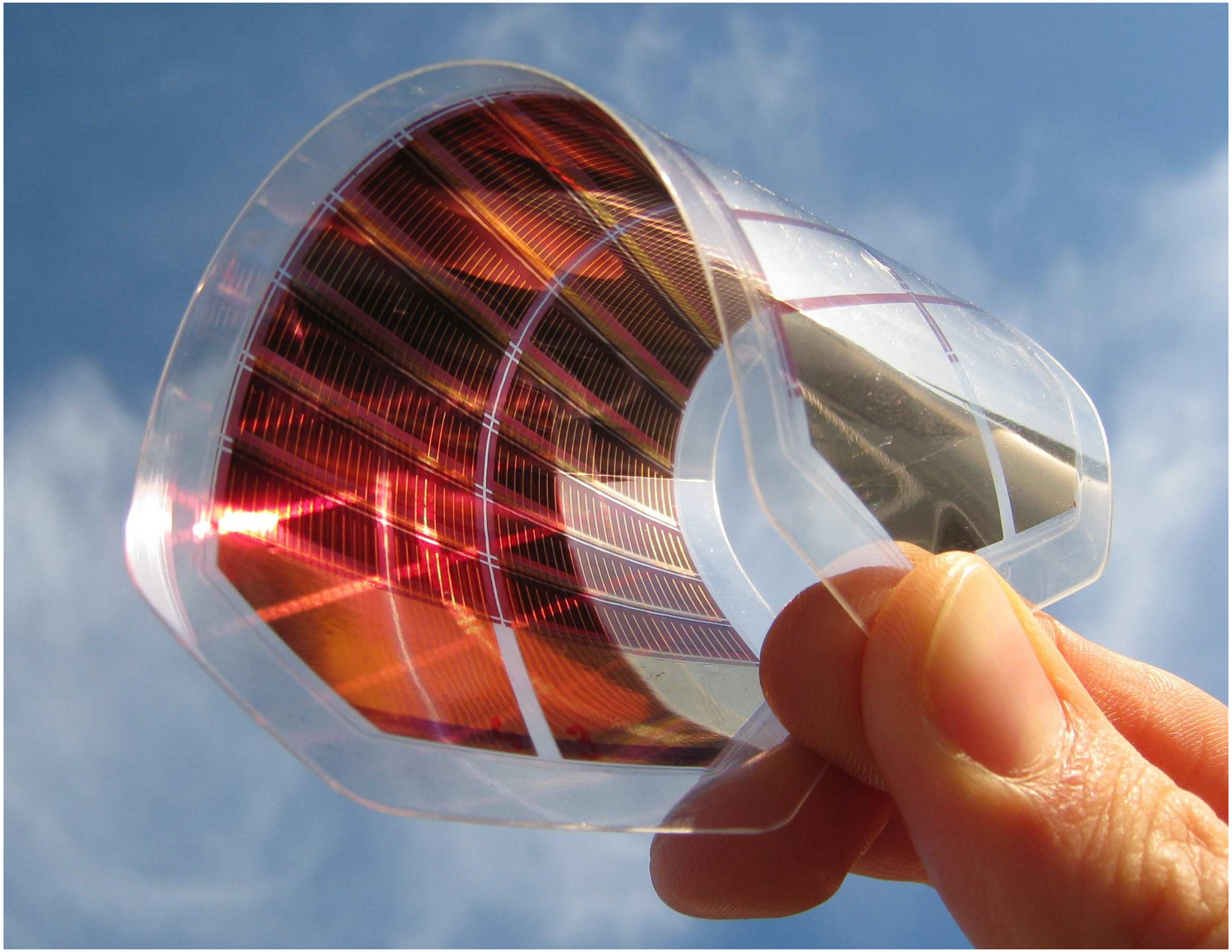
[1] ©Fraunhofer ISE

Organic solar cells

Step 1: Microscopic structure

Organic solar cells



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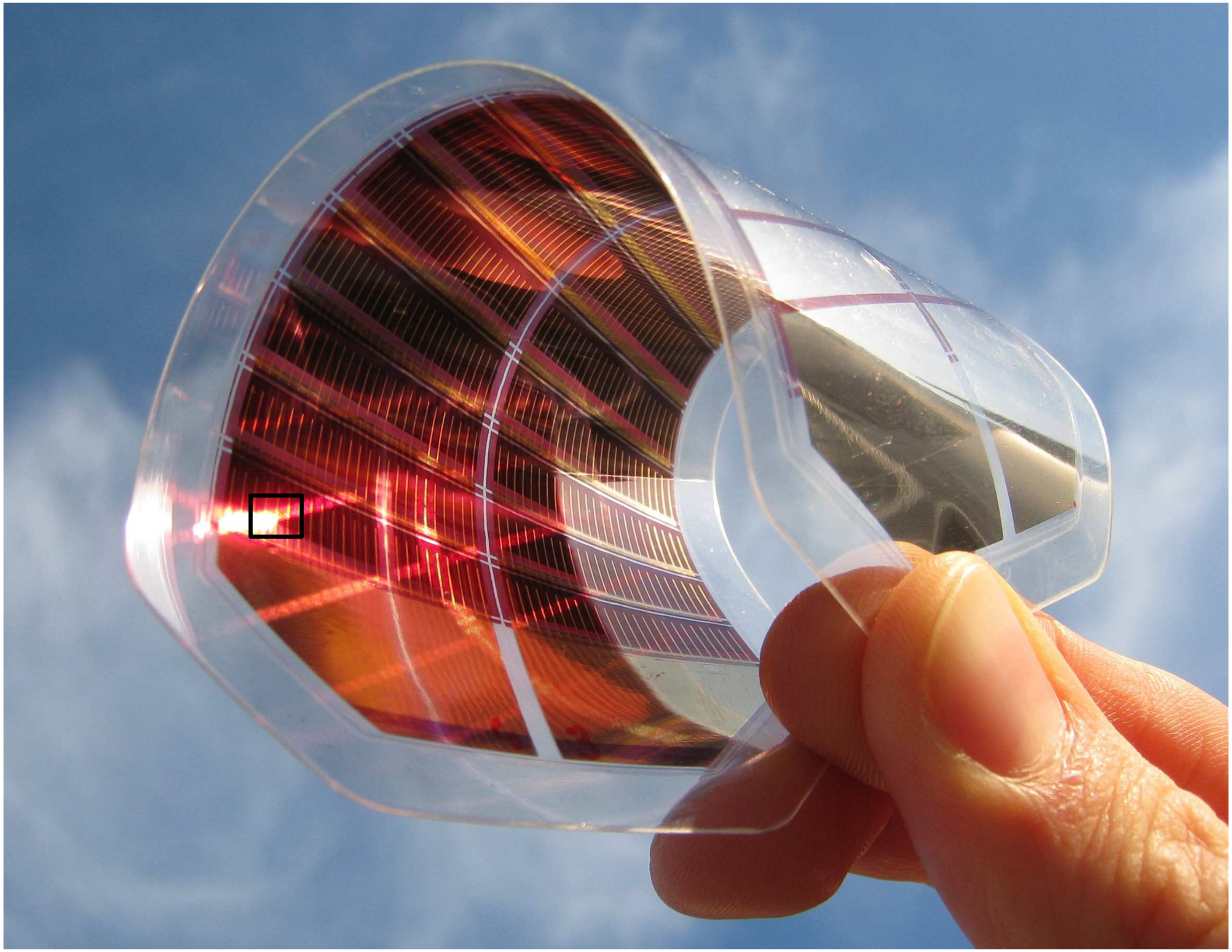

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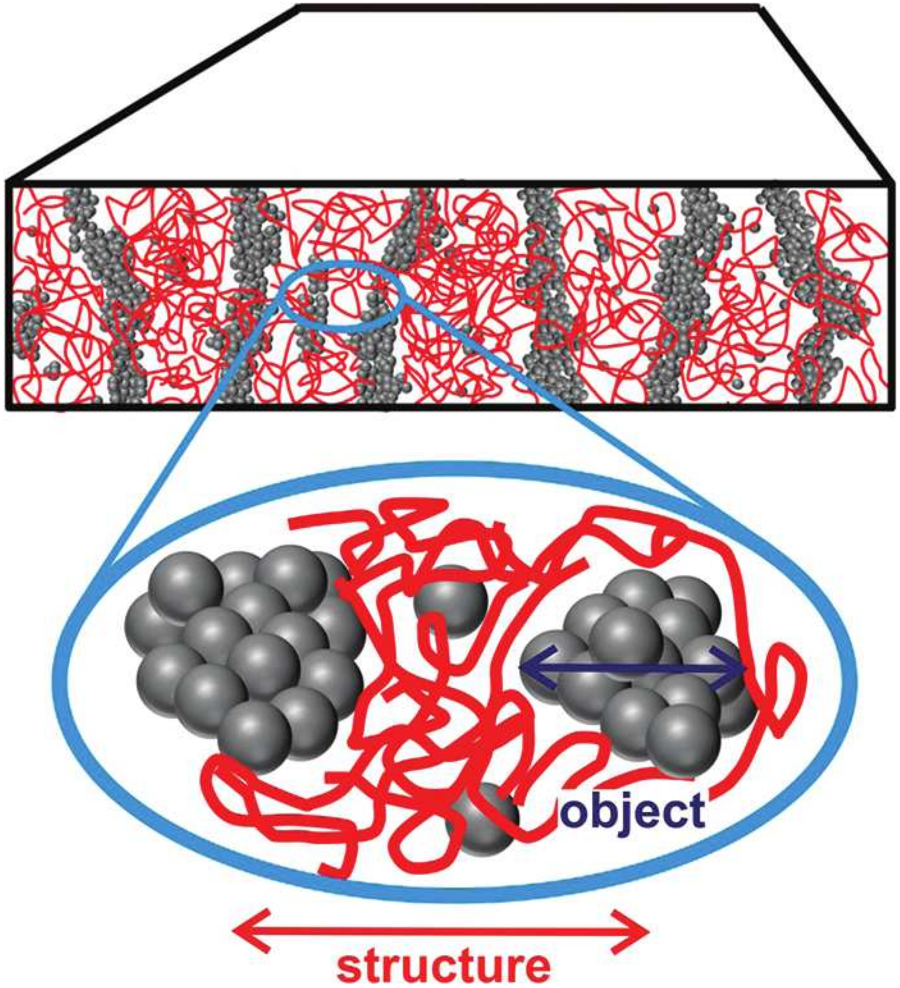

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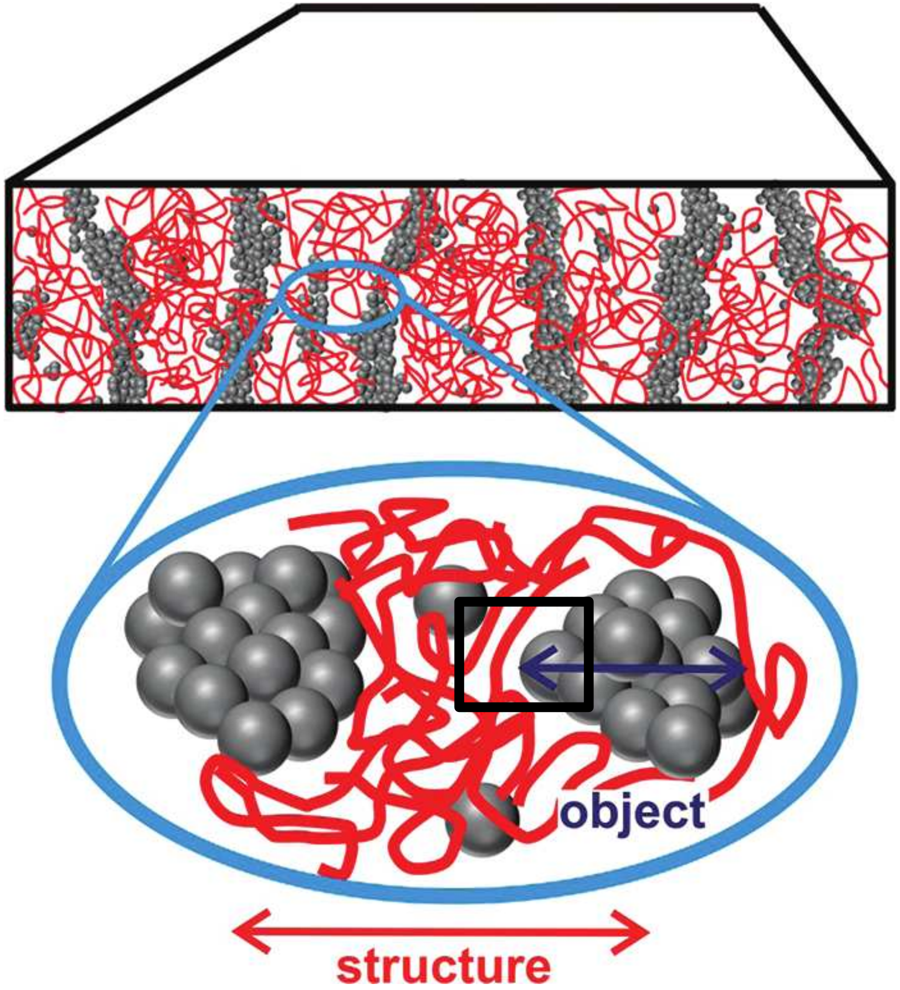

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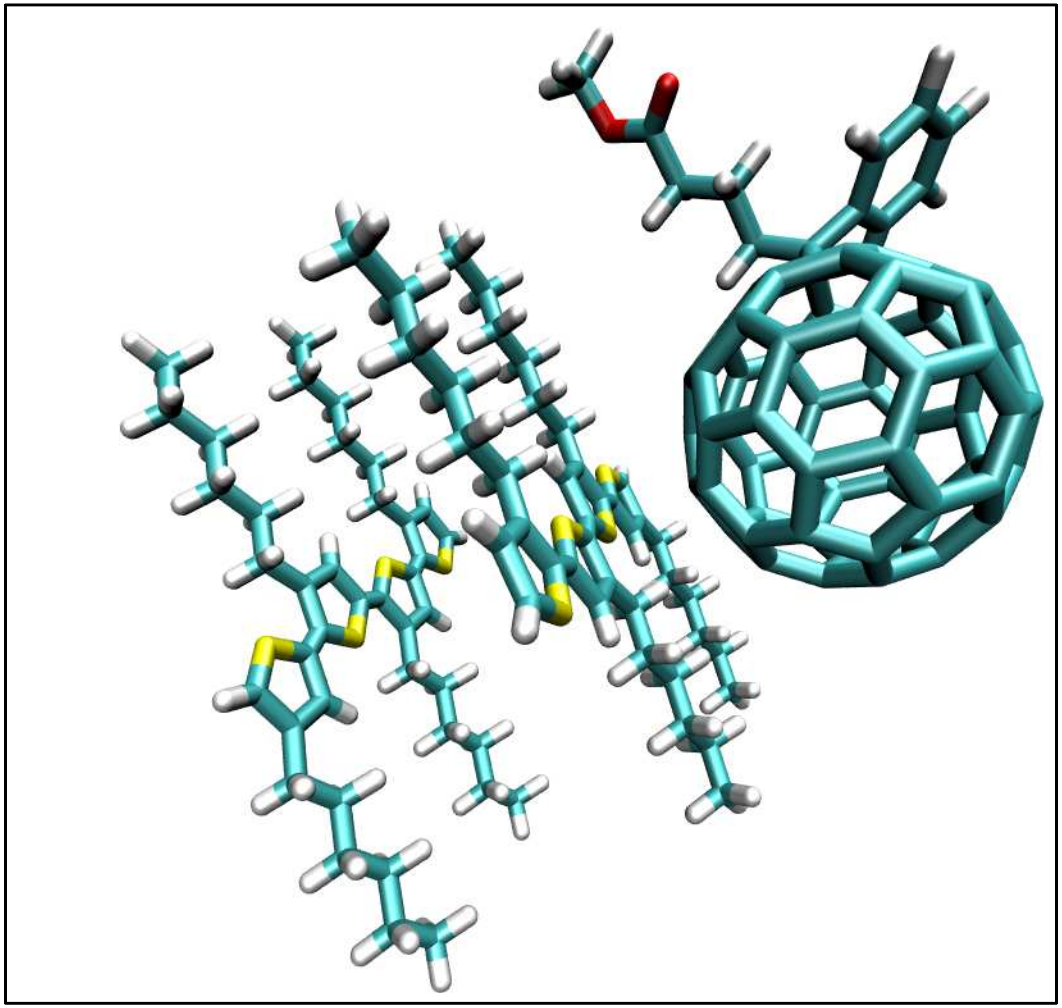

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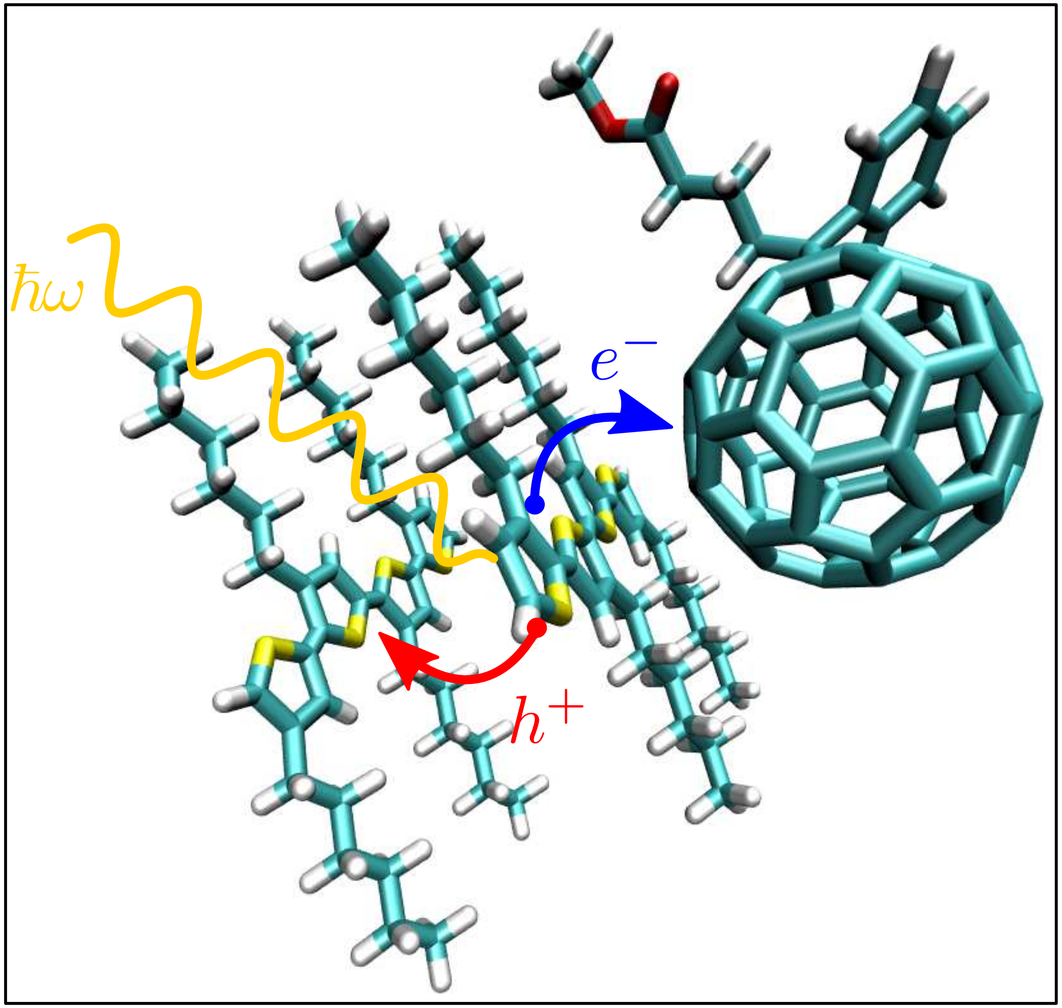

Loss mechanisms

Efficiency of solar→electrical energy conversion very low.

Most prominent loss mechanisms:

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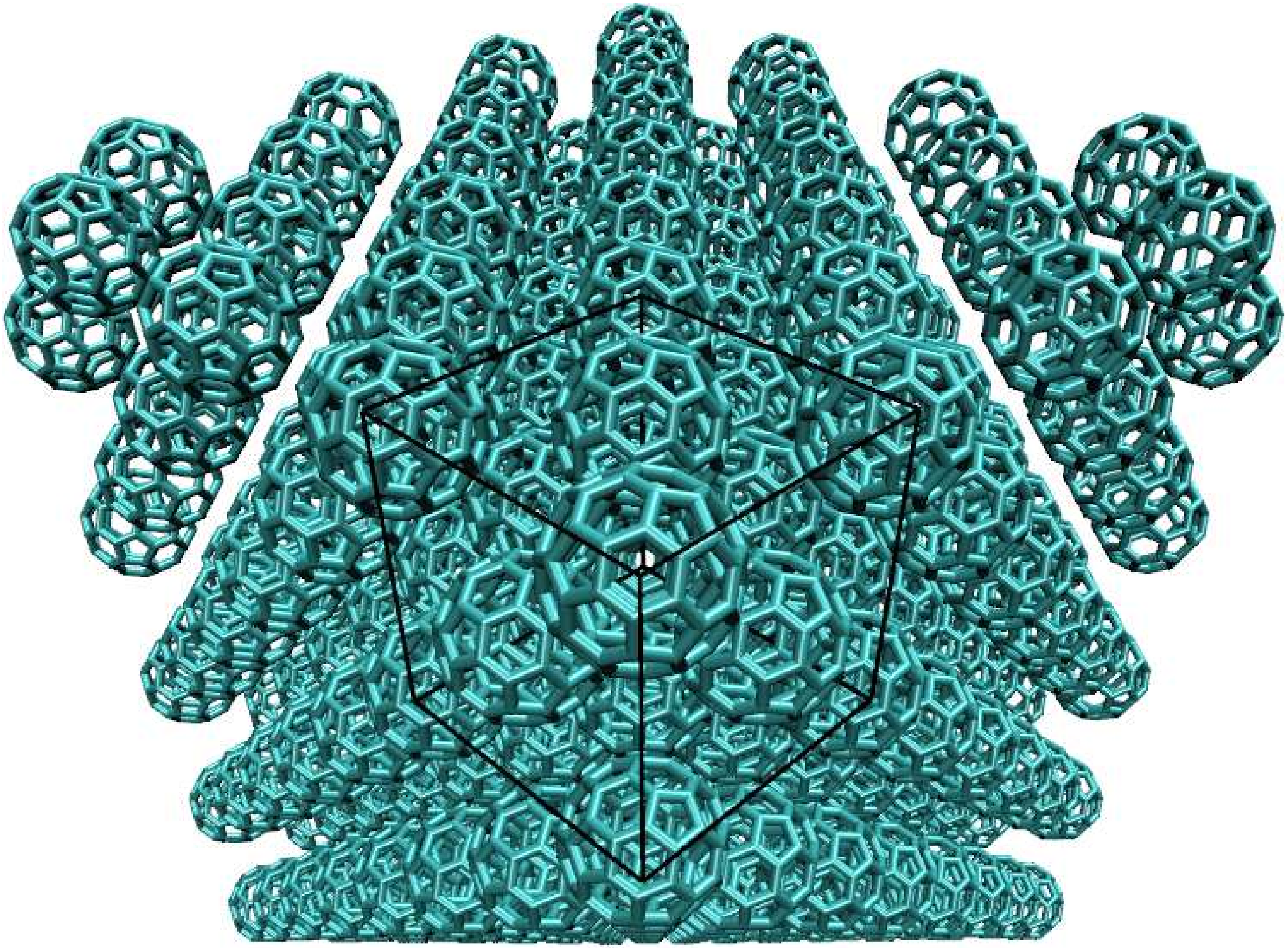
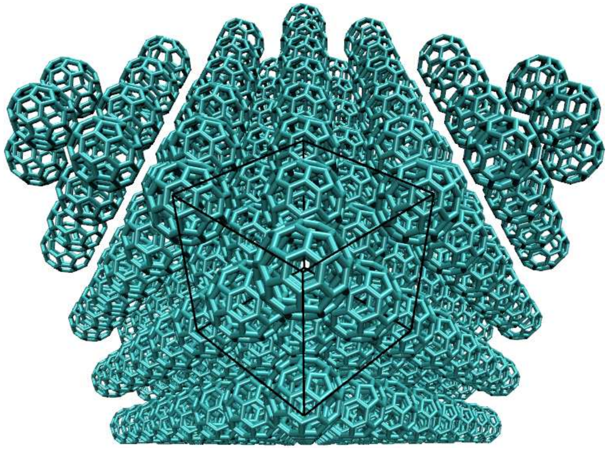
The Aim

Predict electron mobility in a macroscopic fullerene crystal.



Fullerene Crystals

C60



Below $250\mathrm{K}$, C_{60} crystals are stable in FCC configuration and exhibit no special features.

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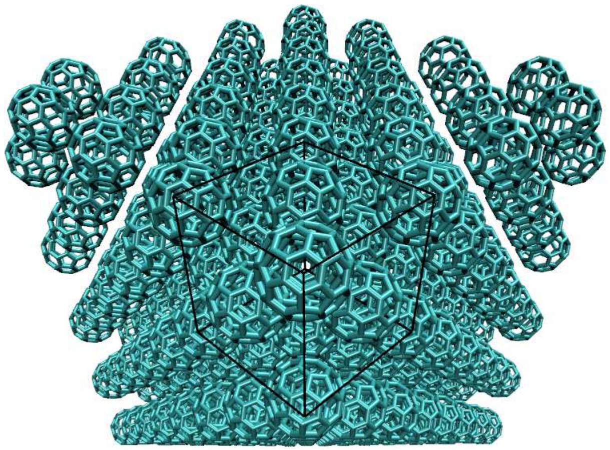

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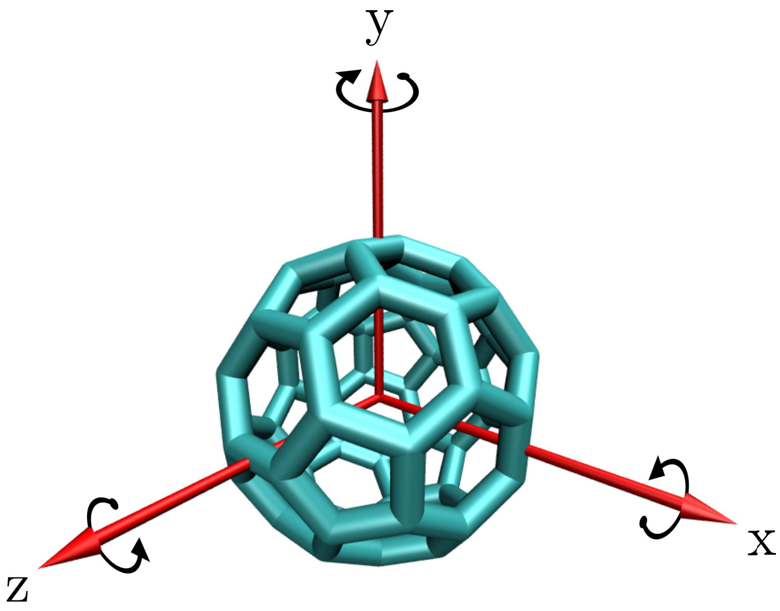
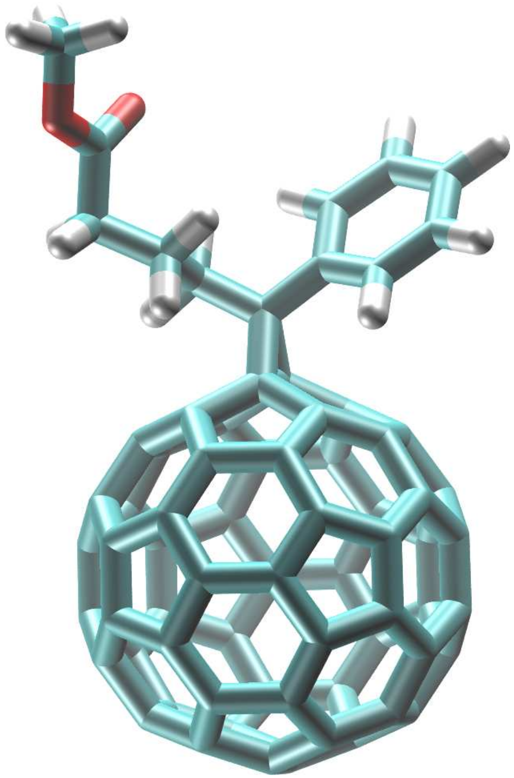
Over $250\mathrm{K}$ every C$_{60}$ molecules pseudo-rotates at its site.



Simulations need to consider these different regimes.

Fullerene Crystals

Phenyl-C61-butyric acid methyl ester (PCBM)



At room temperature crystal structure depends on preparation method.

Observed PCBM crystals are:

- SC
- BCC
- Hexagonal
- Monoclinic
- Triclinic

The Approach

The mobility of an electron can be defined as the derivative of the drift velocity $\mathbf{v}$ with respect to the applied external field $\mathbf{E}$:

$$\boxed{\mu_{ij} = \frac{\partial \left\langle v_i(\mathbf{E}) \right\rangle}{\partial E_j}}$$

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→ how do electrons move?

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Electrons are localised in the form of **polarons** and move via **hopping**.

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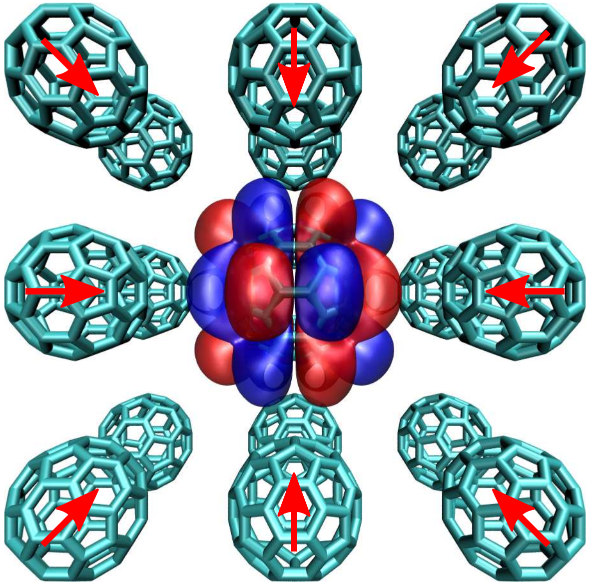

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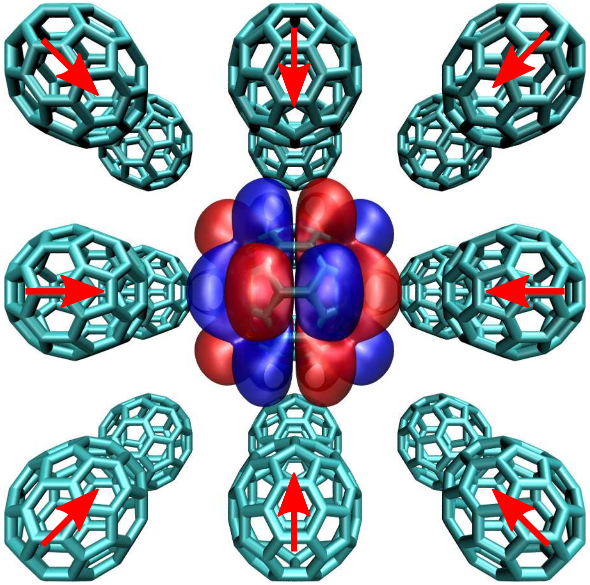

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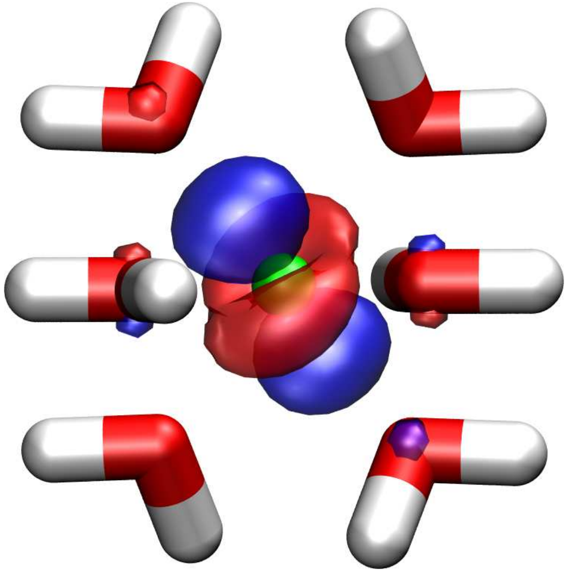

Polaron in water

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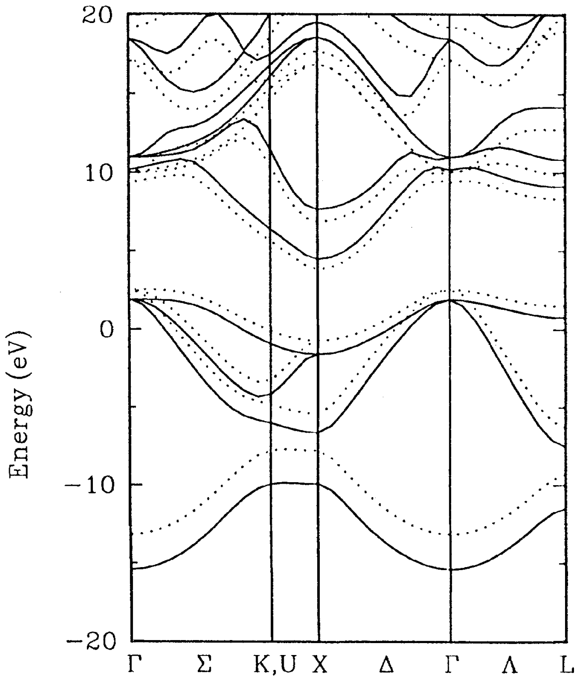


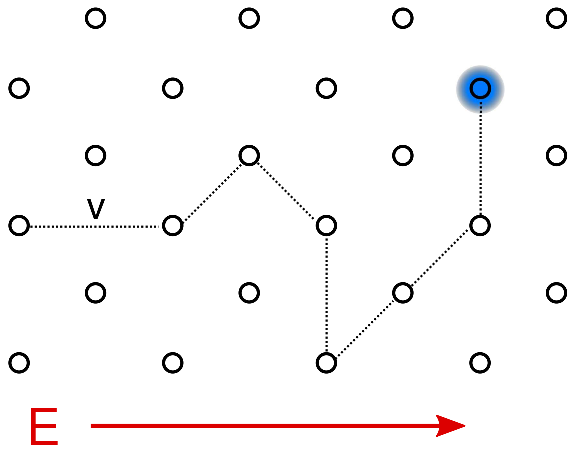
Semiconductor band structure

Wenzien, Käckell, Bechstedt, Cappellini,
PRB **52** 10897 (1995)

Hopping

Hopping model:

Need derivative of average drift velocity $\langle \mathbf{v} \rangle$.



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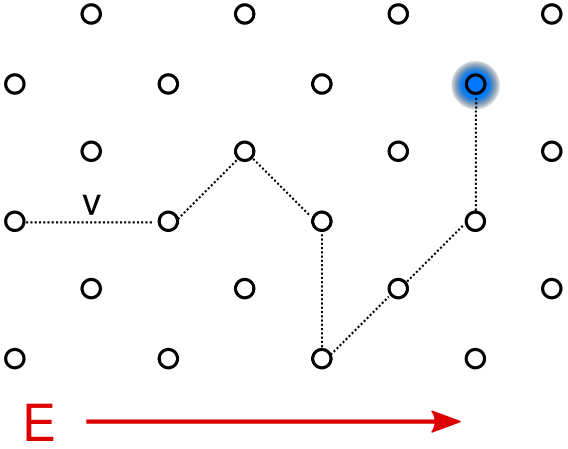
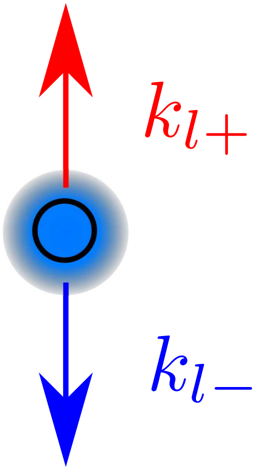


Within hopping model this is given as the sum of all forward and backward hops in each direction. Determined by rate k_l and hopping distance $\mathbf{d}_l$



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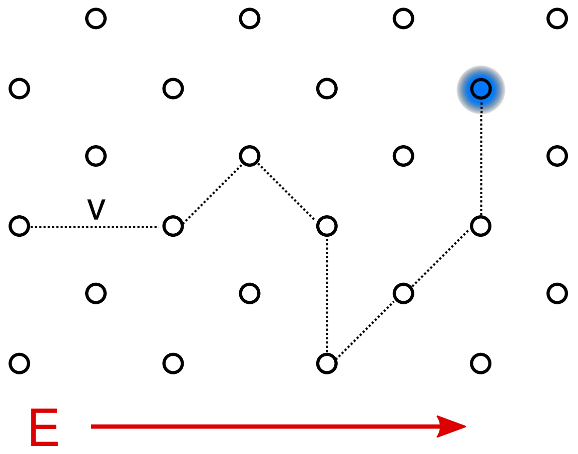

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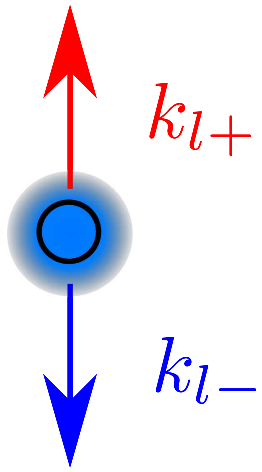
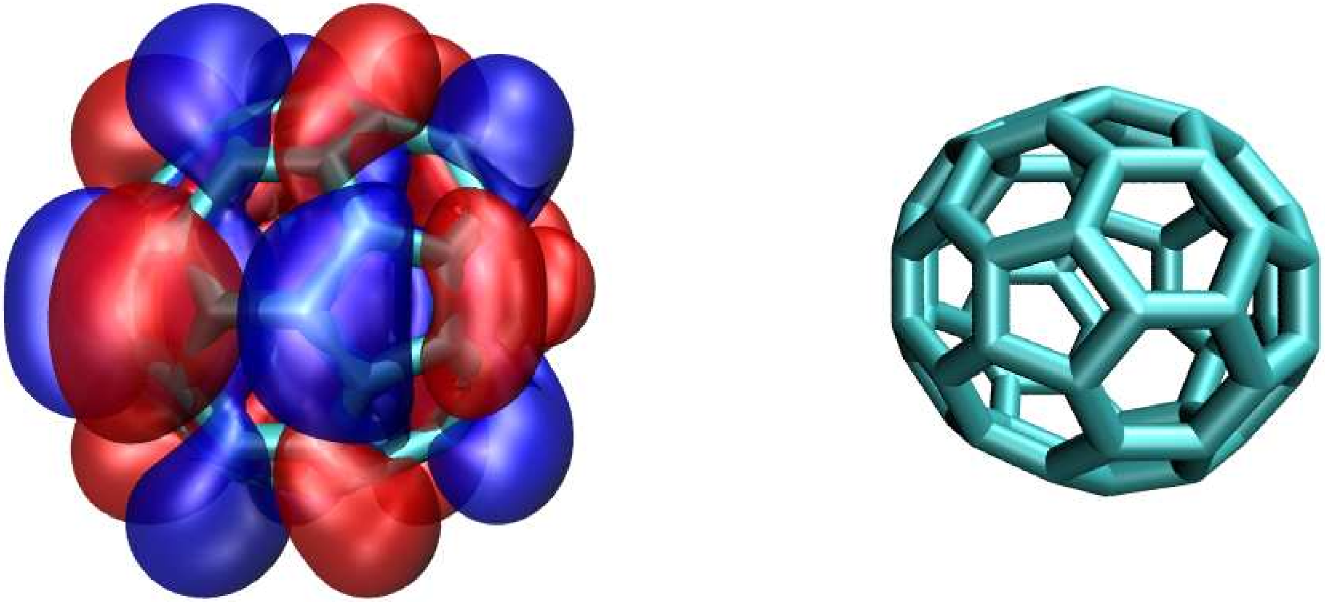


$$\mu_{ij} = \frac{\partial \langle v_i \rangle}{\partial E_j} = \sum_l \frac{\partial \langle k_l \rangle}{\partial E_j} d_{li}$$

Can be solved analytically for crystals.

Hopping

Within the hopping model we need to be able to predict electron transfer rates[1] between nearest and next-nearest neighbours.



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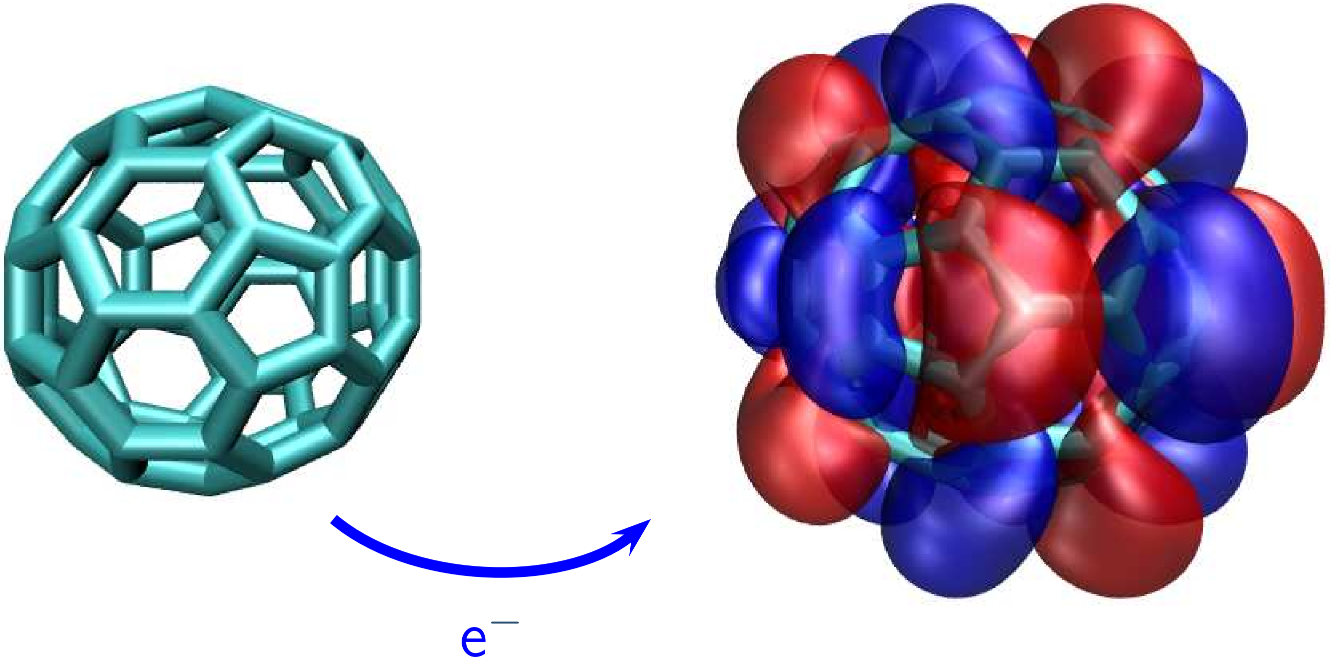

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Rate equations

Rate expressions of the form:

$$\boxed{k = A \times e^{-G/k_{\mathrm{B}}T}}$$

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$\rightarrow$ **semi-classical Landau Zener transition state theory:**
$A = \kappa_{\mathsf{el}}(H_{\mathsf{ab}}, \lambda, \nu_n; T)\nu_n,\ G = \Delta E^{\ddagger} - \Delta(H_{\mathsf{ab}}, \lambda, \Delta G)$

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→ **adiabatic rate:** $A = \nu_n$, $G = \Delta E^\ddagger - \Delta(H_\mathrm{ab}, \lambda, \Delta G)$
valid for $\kappa_\mathrm{el} \approx 1$ $(|H_\mathrm{ab}|^2 >> h\nu_n\sqrt{\lambda k_\mathrm{B}T})$

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Example: Marcus Theory

Marcus theory[1] of electron transfer gives a configuration dependent rate:

$$\boxed{k_{\mathsf{ET}}(\mathbf{r}) = \frac{1}{h}\left\langle |H_{\mathsf{ab}}(\mathbf{r})|^2 \right\rangle \left(4\pi\lambda(\mathbf{r}) k_{\mathsf{B}} T\right)^{-1/2} e^{-(\lambda(\mathbf{r})-\Delta G(\mathbf{r}))/4\lambda(\mathbf{r}) k_{\mathsf{B}} T}}$$

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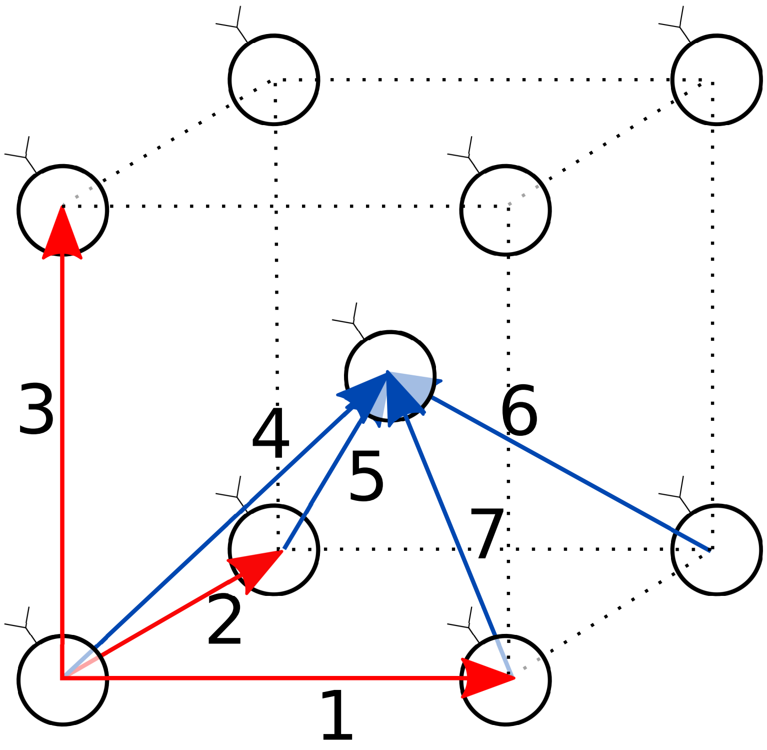

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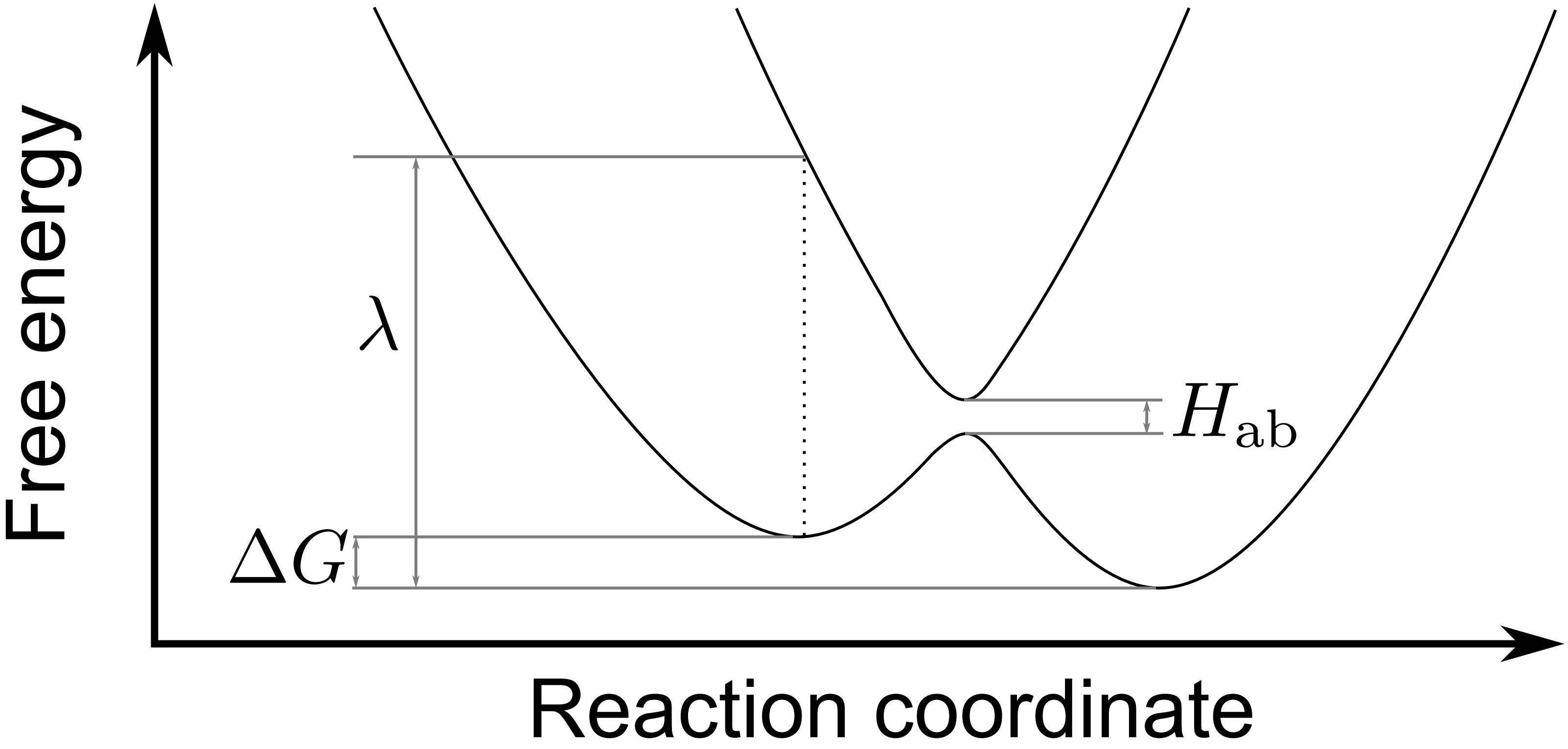

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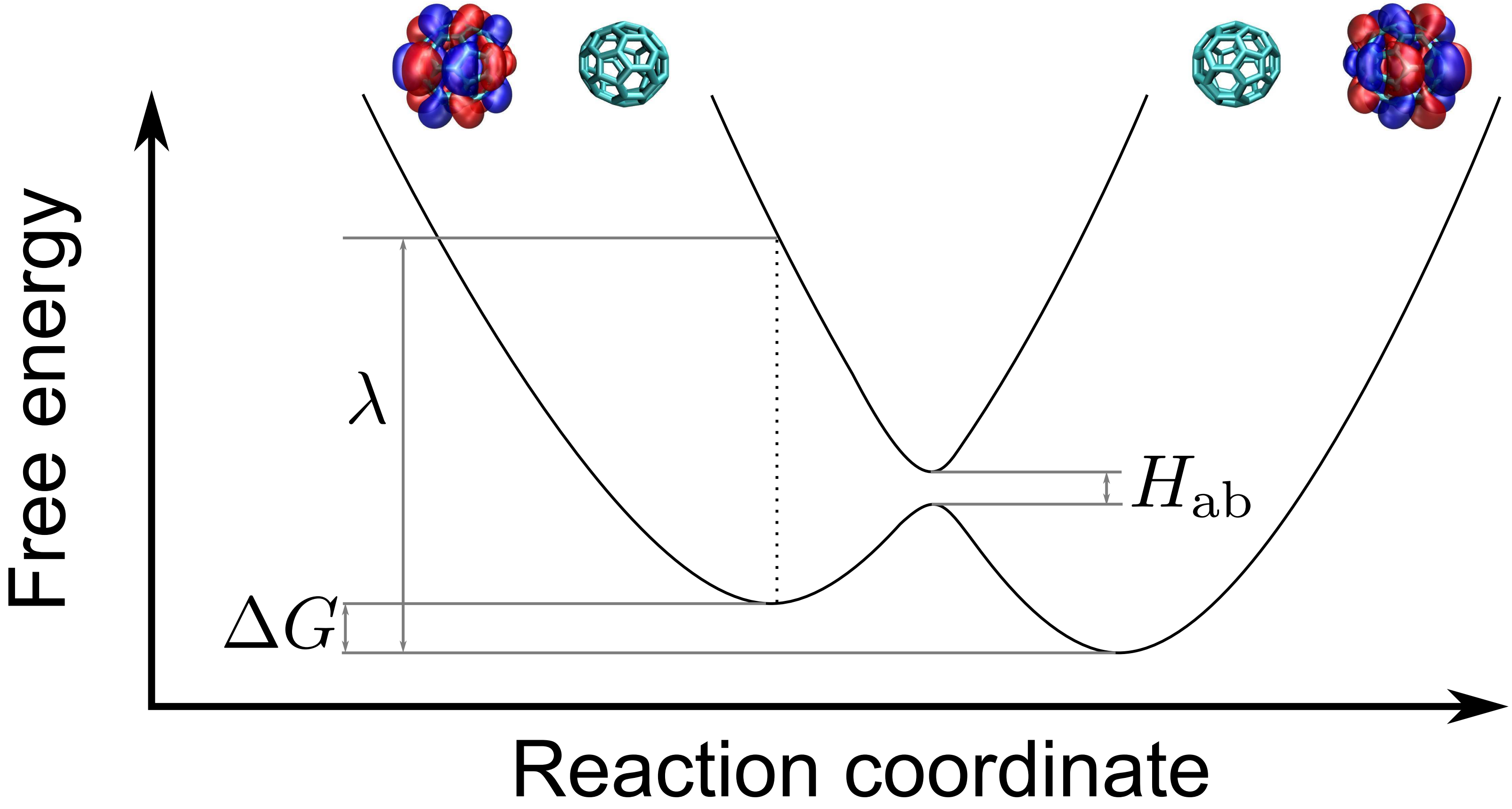

Diabatic states: Charges localised on either Donor or Acceptor molecules.

Concerning the reaction coordinate

Charge of Donor or acceptor is not a good reaction coordinate!
Actual charge hopping not the slow process.

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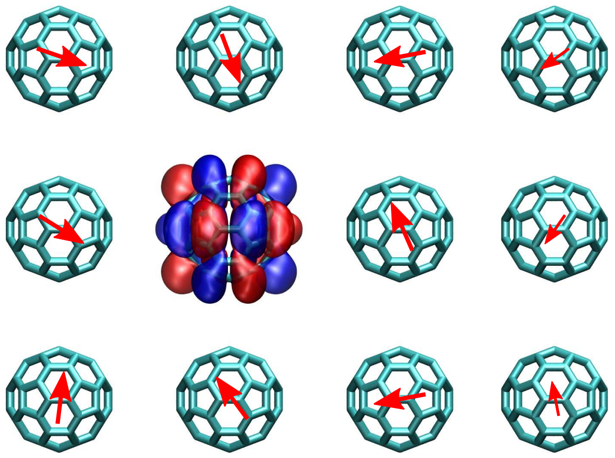

Electron localised on a site,
➔ surroundings polarised but not necessarily in minimum

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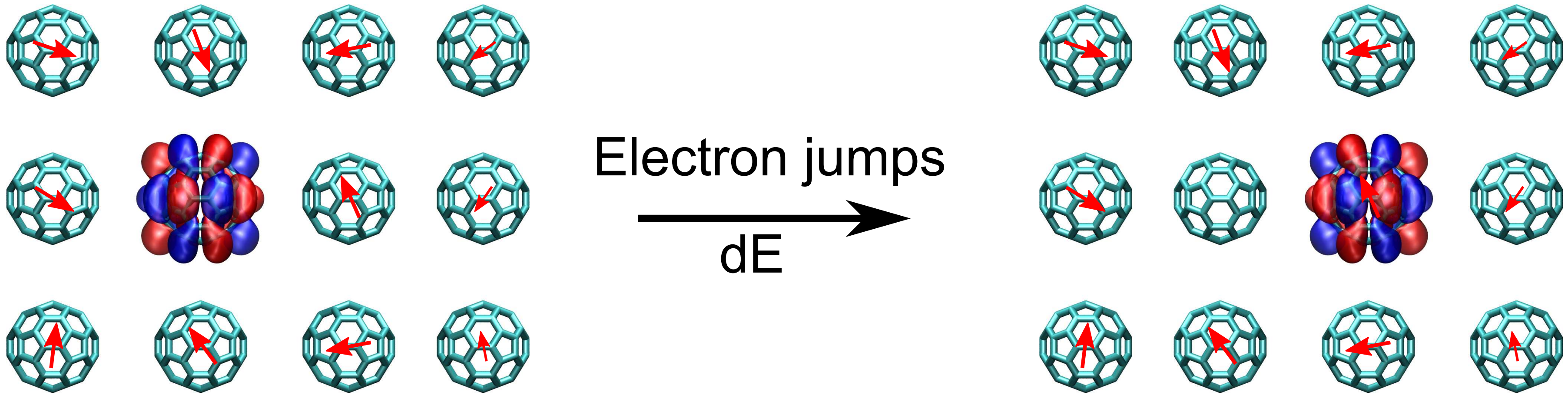

Surroundings still polarised for old charge state

How to calculate the parameters

Need to construct the charge localised states.

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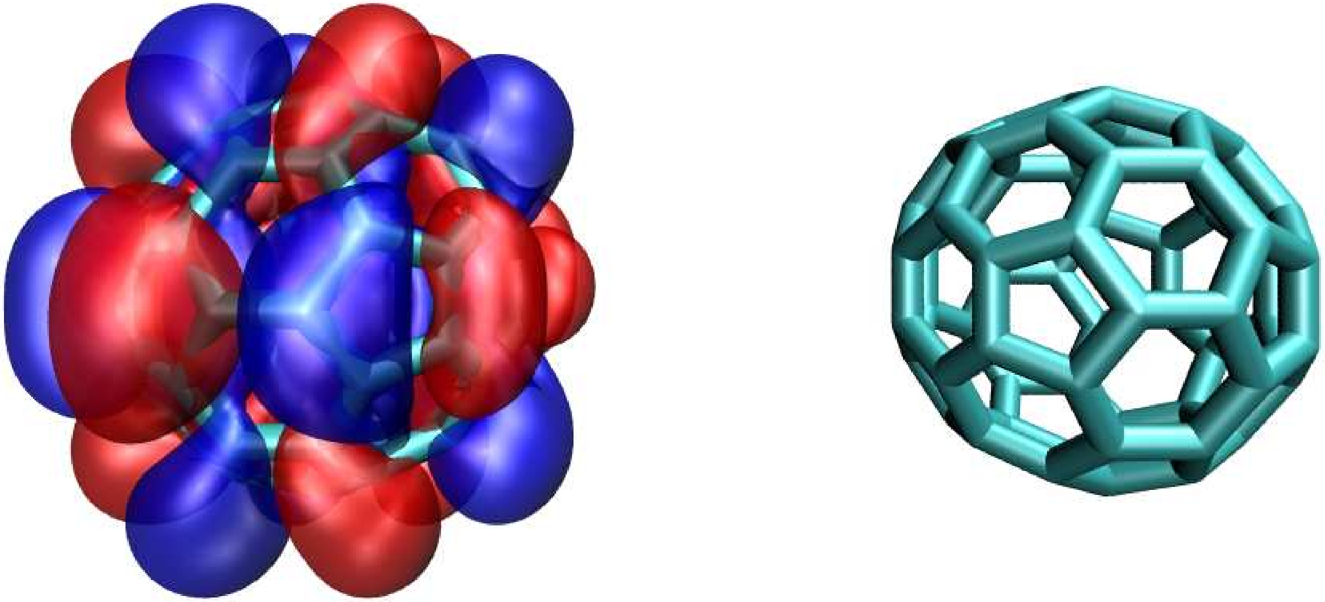
Instead of this:



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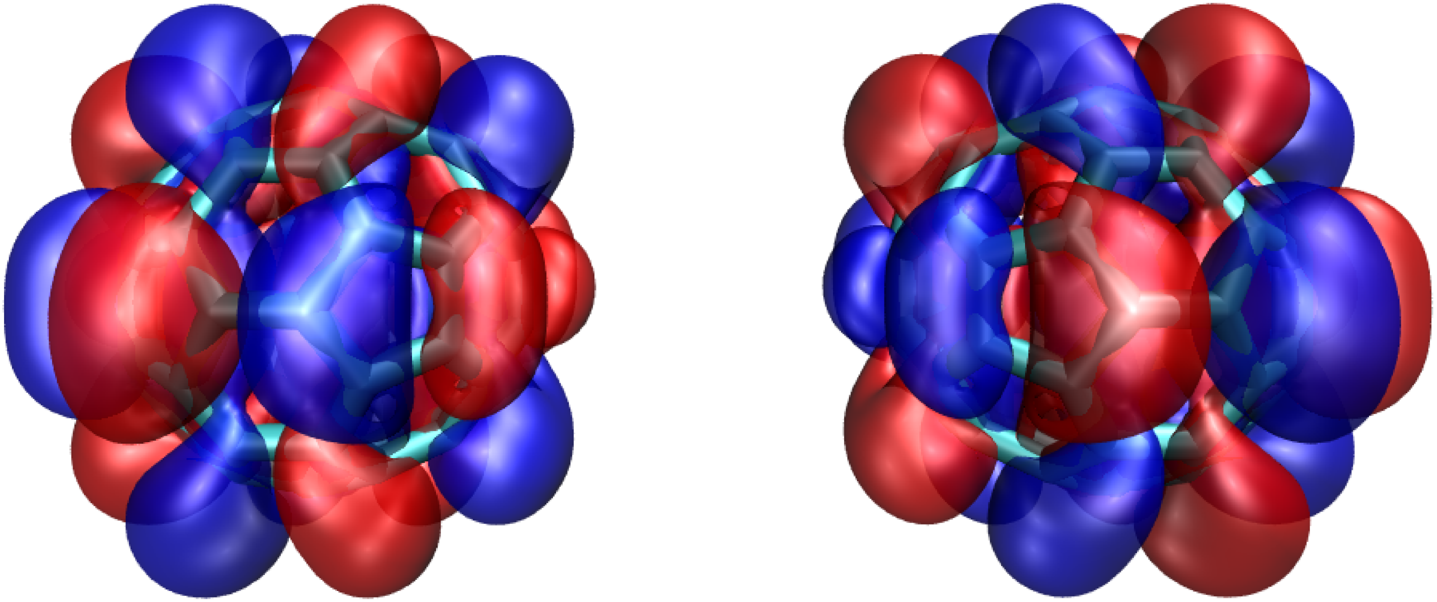
DFT will always give this (even with hybrid functionals):



Methods

To circumvent the delocalisation error we use:

Constrained DFT:

- B. Kaduk, T. Kowalczyk, and T. Van Voorhis, Chem. Rev. **112** 321 (2011)
- H. Oberhofer and J. Blumberger J. Chem. Phys. **131** 64101 (2009)
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Fragment orbital DFT

- H. Oberhofer and J. Blumberger Angew. Chem. Int. Ed. **49** 3631 (2010)
- K. Senthilkumar, F. C. Grozema, F. M. Bickelhaupt, L. D. A. Siebbeles, J. Chem. Phys. **119** 9809 (2003)
- A. Farazdel, M. Dupuis, E. Clementi, A. Aviram, JACS **112** 4206 (1990)

Constrained Density Functional Theory

$$w_{\mathsf{A,D}} = w_{\mathsf{D}} - w_{\mathsf{A}} = \frac{\sum_{i\in\mathsf{D}} \rho_i(\mathbf{r}-\mathbf{R}_i) - \sum_{i\in\mathsf{A}} \rho_i(\mathbf{r}-\mathbf{R}_i)}{\sum_{i=1}^{N} \rho_i(\mathbf{r}-\mathbf{R}_i)}$$

A constraint on charges takes the form [1]

$$\int w(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} - N_{\mathsf{c}} = 0$$

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[1] Q. Wu and T. van Voorhis, Phys. Rev. A **72** 024502 (2005)

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With a new energy functional

$$F[\rho, V] = E[\rho] + V(\int w(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} - N_{\mathsf{c}})$$

---

[1] Q. Wu and T. van Voorhis, Phys. Rev. A **72** 024502 (2005)

Constrained Density Functional Theory

$$w_{\mathsf{A,D}} = w_{\mathsf{D}} - w_{\mathsf{A}} = \frac{\sum_{i\in\mathsf{D}} \rho_i(\mathbf{r}-\mathbf{R}_i) - \sum_{i\in\mathsf{A}} \rho_i(\mathbf{r}-\mathbf{R}_i)}{\sum_{i=1}^{N} \rho_i(\mathbf{r}-\mathbf{R}_i)}$$

A constraint on charges takes the form [1]

$$\int w(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} - N_{\mathsf{c}} = 0$$

With a new energy functional

$$F[\rho, V] = E[\rho] + V(\int w(\mathbf{r})\rho(\mathbf{r})\, d\mathbf{r} - N_{\mathsf{c}})$$

The matrix element is then given by:

$$\boxed{H_{\mathsf{ab}} \propto \langle\psi_{\mathsf{a}}|\, H_{\mathsf{KS}}\, |\psi_{\mathsf{b}}\rangle = F_{\mathsf{B}}\, \langle\psi_{\mathsf{a}}|\psi_{\mathsf{b}}\rangle - V_{\mathsf{B}}\, \langle\psi_{\mathsf{a}}|\, w\, |\psi_{\mathsf{b}}\rangle}$$

---

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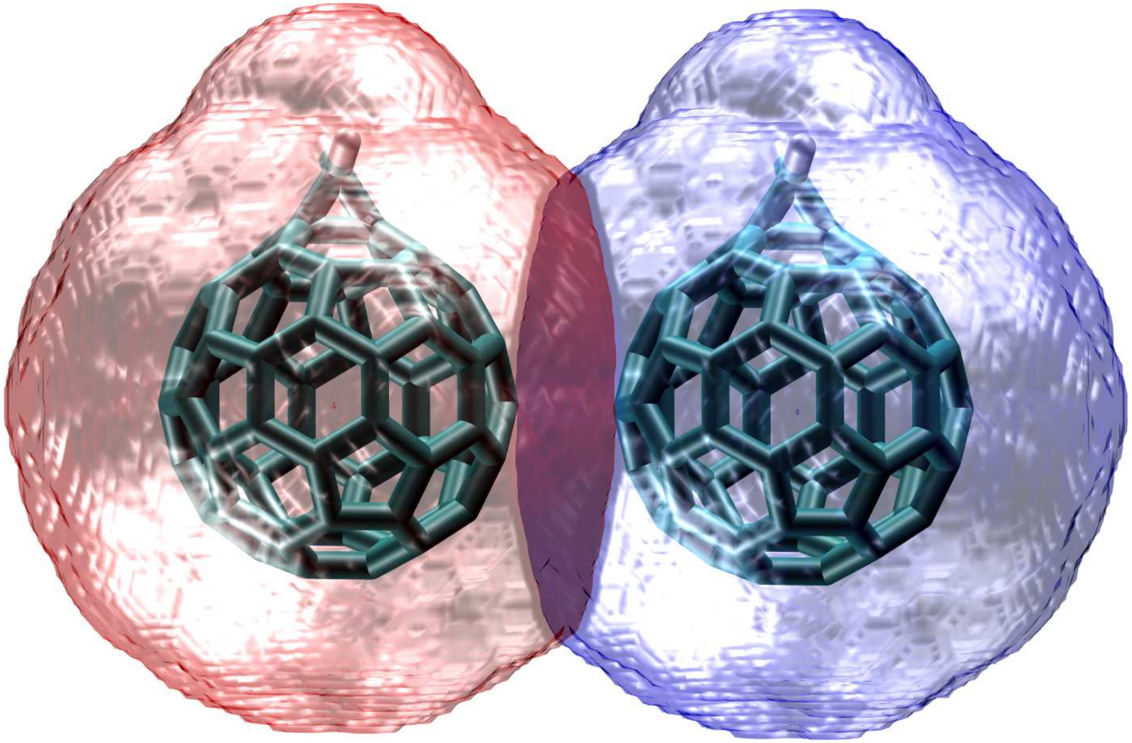

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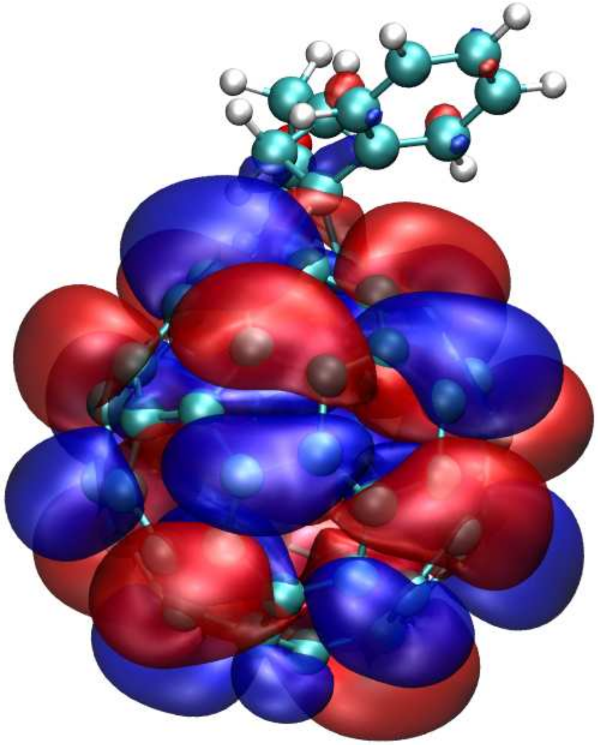
[1] H. Oberhofer and J. Blumberger J. Chem. Phys. **131** 64101 (2009)

Fragment Orbital DFT

Separate donor and Acceptor group and calculate the HOMO's of the charged groups separately.



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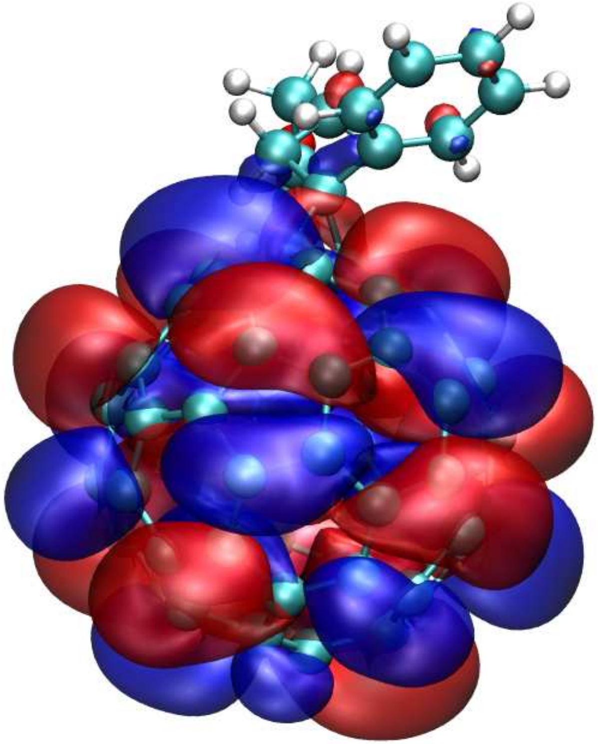

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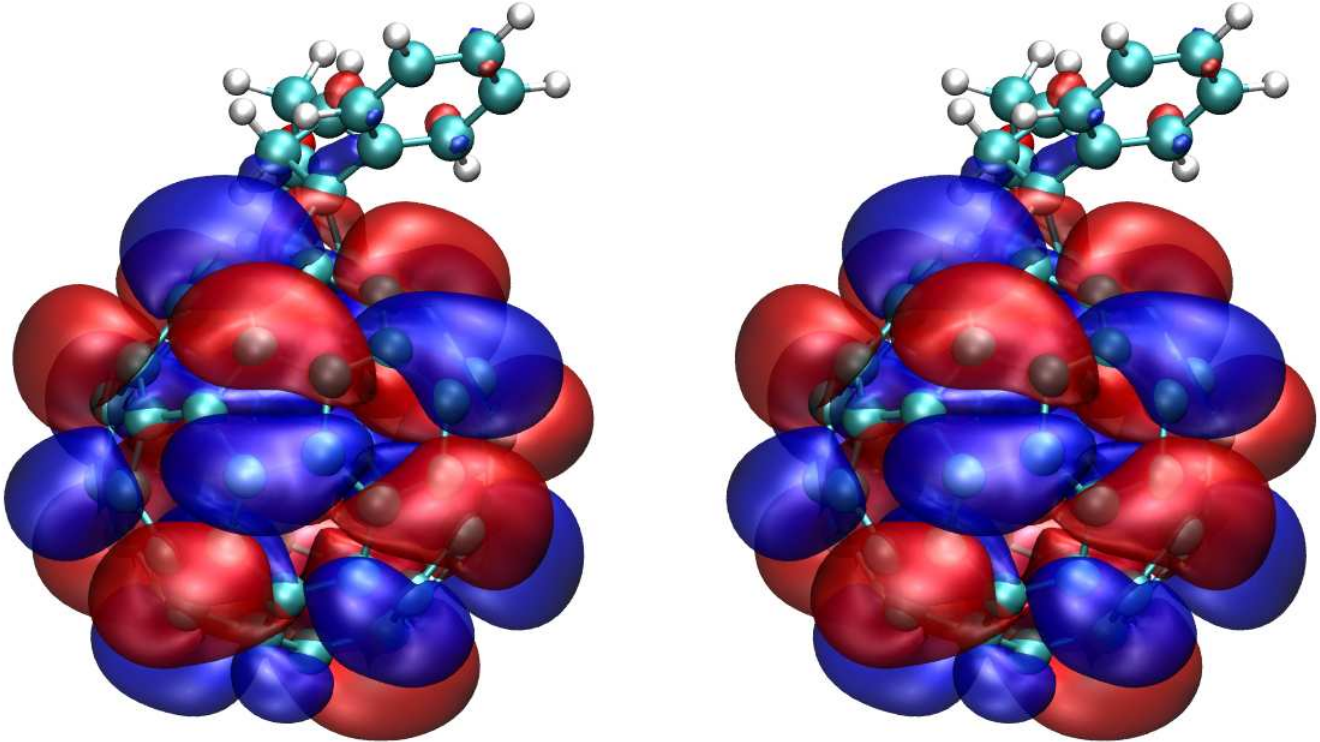
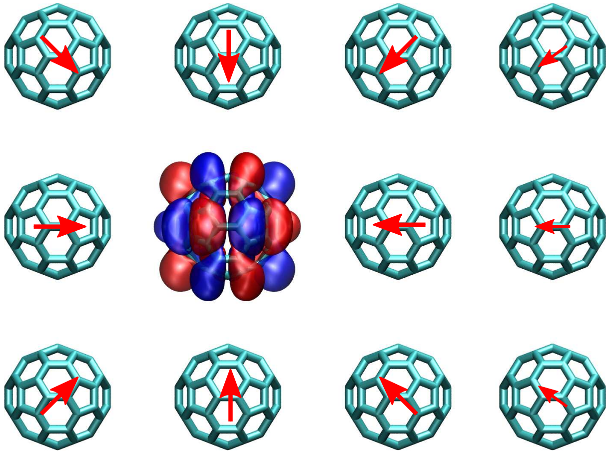


H_{ab} is the off-diagonal Kohn-Sham matrix element of the two HOMO's.

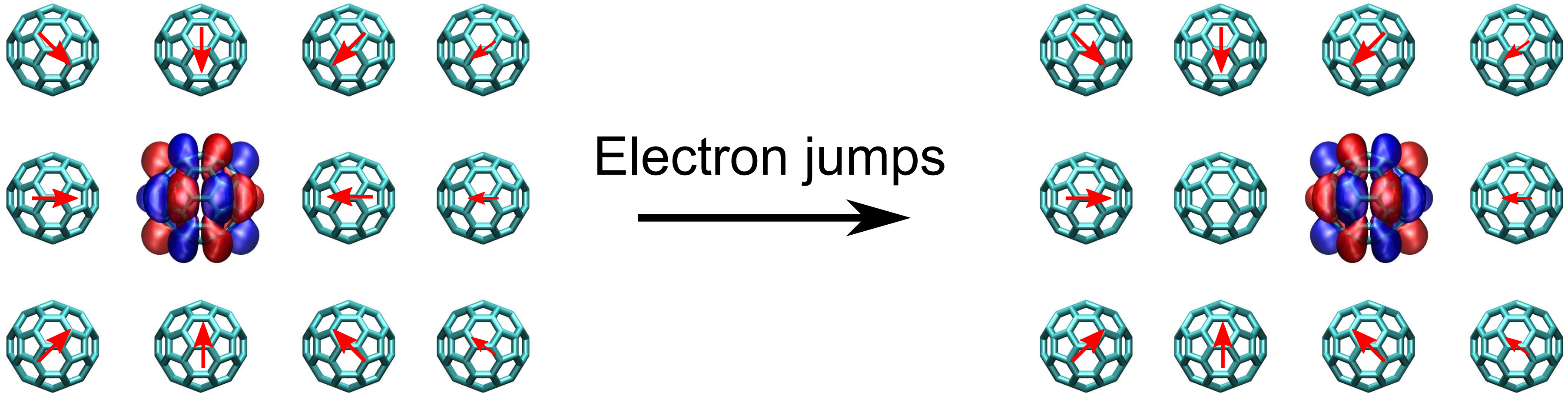
$$H_{\mathrm{ab}} \propto \left\langle \Phi_{\mathrm{a}}^{\mathrm{HOMO}} \right| H_{\mathrm{KS}} \left| \Phi_{\mathrm{b}}^{\mathrm{HOMO}} \right\rangle$$

Reorganisation energy



Diabatic state a

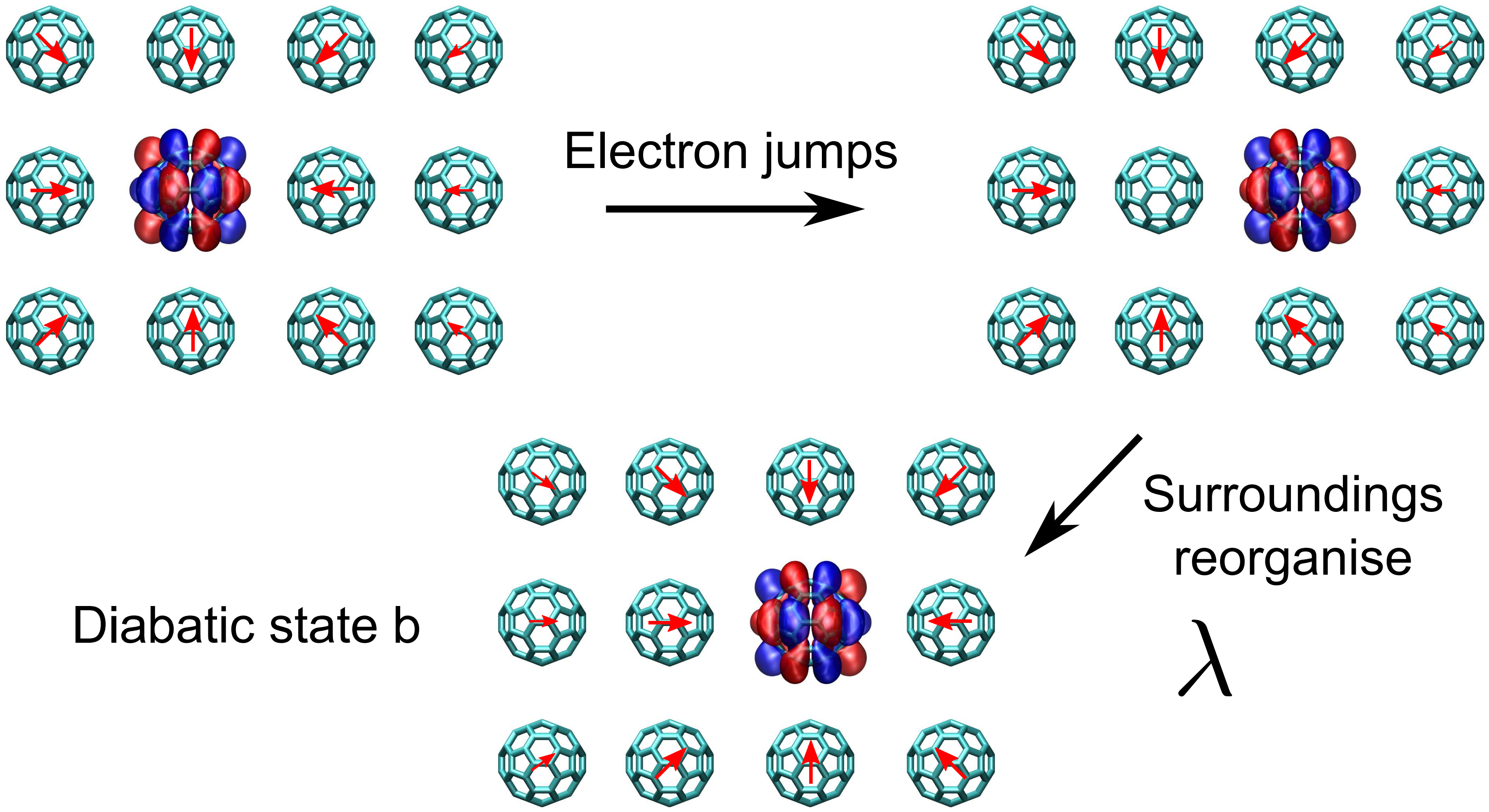
Reorganisation energy



Electron jumps

Surroundings still
polarised for
old charge state

Reorganisation energy



Electron jumps

Surroundings reorganise

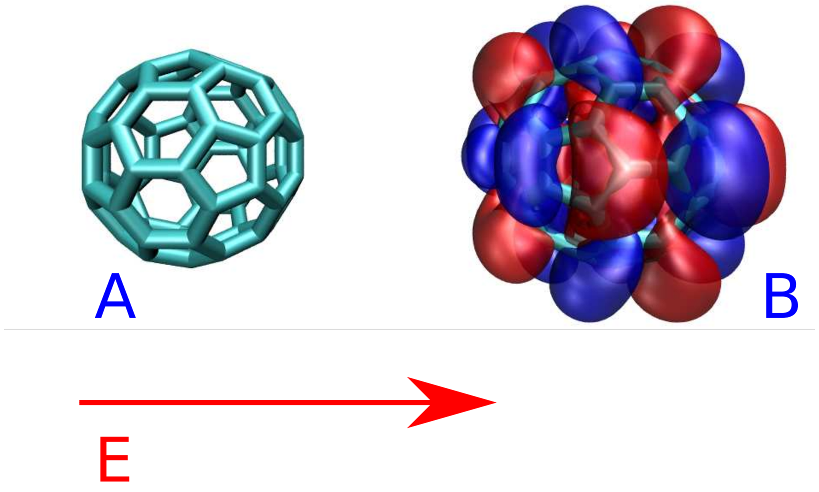
λ

Diabatic state b

Driving force of the hopping reaction

- In an ideal bravais crystal all sites are equivalent.
- Only with an external potential ΔG is non-zero.
- Given an external Field $\mathbf{E}$ the energy difference between two lattice sites A and B is simply:

$$\Delta G_{\mathrm{A,B}} = -e\mathbf{E}.(\mathbf{r}_{\mathrm{B}} - \mathbf{r}_{\mathrm{A}}) = -e\mathbf{E}.\mathbf{d}_{\mathrm{AB}}$$

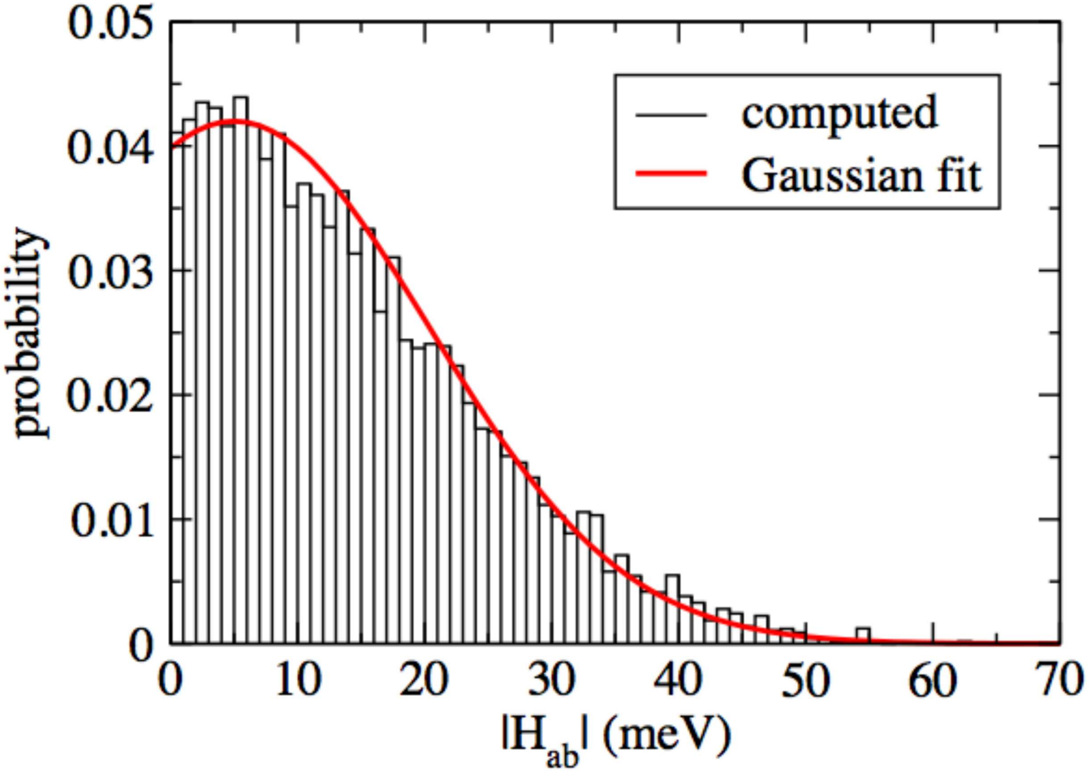


Some results for hopping in Fullerene crystals

- H. Oberhofer and J. Blumberger, Phys. Chem. Chem. Phys. **14** 13846 (2012)
- F. Gajdos, H. Oberhofer, M. Dupuis, and J. Blumberger J. Phys. Chem. Lett. **4** 1012 (2013)

Results

Distribution of (nearest) site-to-site transition matrix elements in crystal

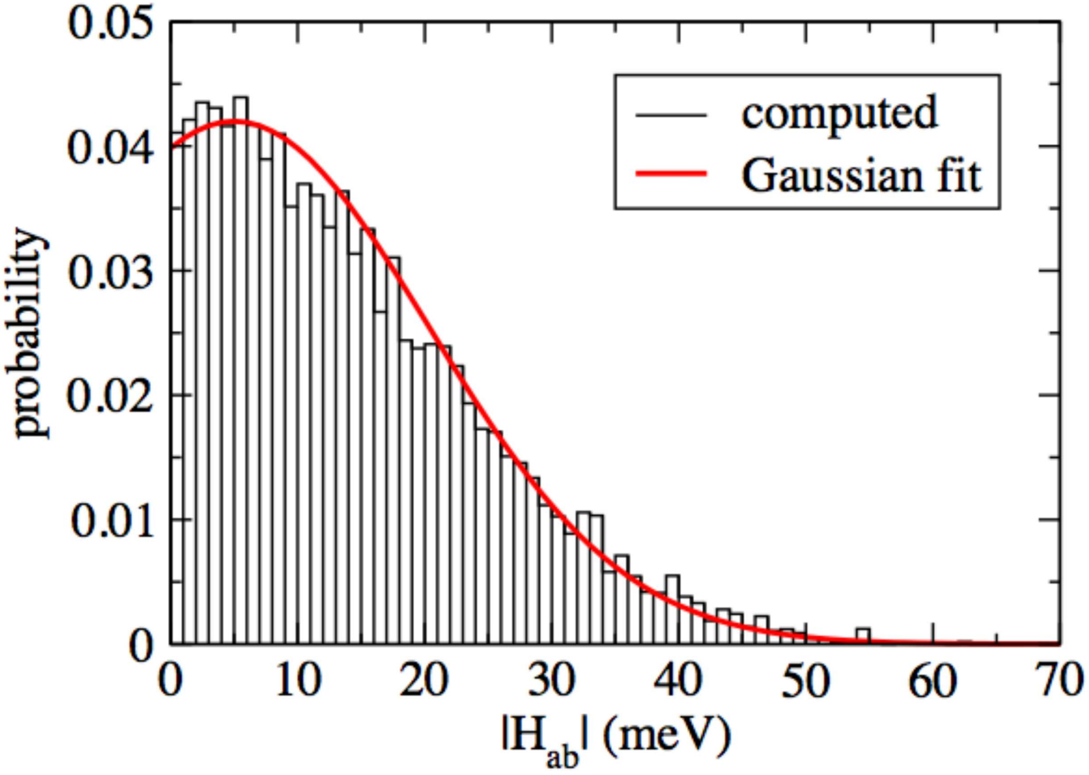


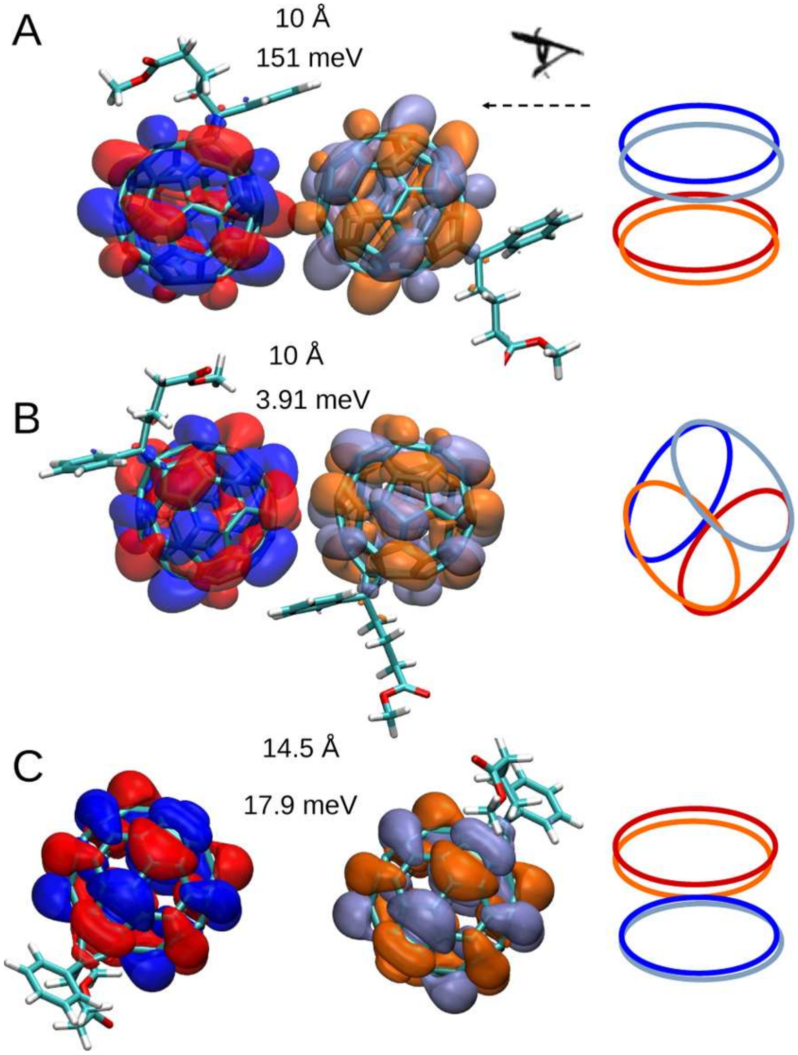
Sampled over ≈ 27000 equidistributed configurations

Gaussian distribution arises from different relative orientations of molecules.

Results

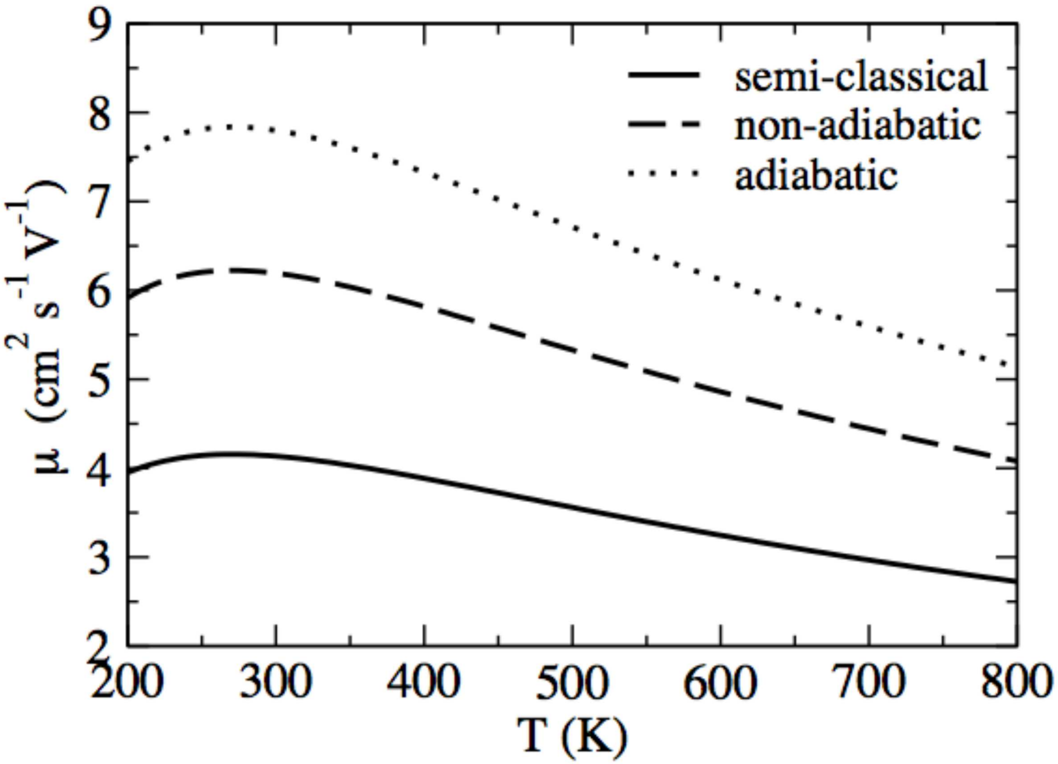
Where do these variations come from?





Results

Temperature dependence of mobilities for different rate equations.



Experimental value $\mu(T = 300\text{K}) = 0.5\text{cm}^2/s/V^1$

---

[1] Frankevich, Maruyamaa, Ogataa, CPL **214** 39, (1993)

Rate equations

Rate expressions of the form:

$$\boxed{k = A \times e^{-G/k_\mathsf{B}T}}$$

→ **semi-classical Landau Zener transition state theory:**
$A = \kappa_\mathsf{el}(H_\mathsf{ab}, \lambda, \nu_n; T)\nu_n$, $G = \Delta E^\ddagger - \Delta(H_\mathsf{ab}, \lambda, \Delta G)$

→ **non-adiabatic (Marcus) rate:** $A \propto |H_\mathsf{ab}|^2(\lambda k_\mathsf{B}T)^{-1/2}$, $G = \Delta E^\ddagger$
valid for activated processes where $\lambda >> H_\mathsf{ab}$

→ **adiabatic rate:** $A = \nu_n$, $G = \Delta E^\ddagger - \Delta(H_\mathsf{ab}, \lambda, \Delta G)$
valid for $\kappa_\mathsf{el} \approx 1$ ($|H_\mathsf{ab}|^2 >> h\nu_n\sqrt{\lambda k_\mathsf{B}T}$)

---

[1] Brunschwig, Logan, Newton, Sutin, JACS, **102**, 5798 (1980)
[2] R. A. Marcus, Rev. Mod. Phys. , **65**, 599 (1993)

Some words on the hopping model

adiabatic or non-adiabatic? Adiabaticity is controlled by ratio:

$$2\pi\gamma = \frac{\pi^{3/2}|H_{\mathsf{ab}}|^2}{h\nu_n\sqrt{k_{\mathsf{B}}T\lambda}}$$

$2\pi\gamma \gg 1$: adiabatic regime
$2\pi\gamma \ll 1$: non-adiabatic regime
here $\langle 2\pi\gamma\rangle = 0.65$!

Some words on the hopping model

adiabatic or non-adiabatic? neither

Are there even charge localised states?

Some words on the hopping model

adiabatic or non-adiabatic? neither

Are there even charge localised states?
Diabatic states exist if there is a finite barrier separating the sites:
In our picture that means $|H_{\mathsf{ab}}| \leq 3\lambda/8$

Some words on the hopping model

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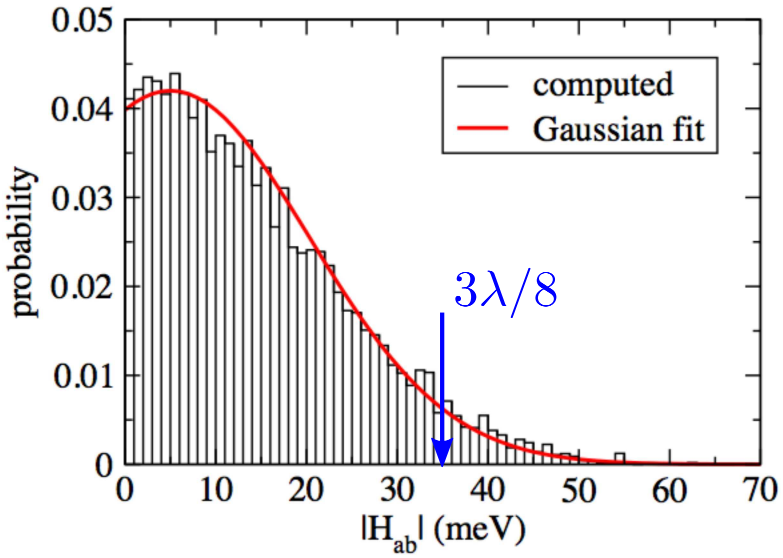

For $\approx$ 5% of all configurations there is no barrier.
Considering nuclear quantum effects (zero point energy)
$\rightarrow$ barrier even lower.

Some words on the hopping model

adiabatic or non-adiabatic? neither

Are there even charge localised states?

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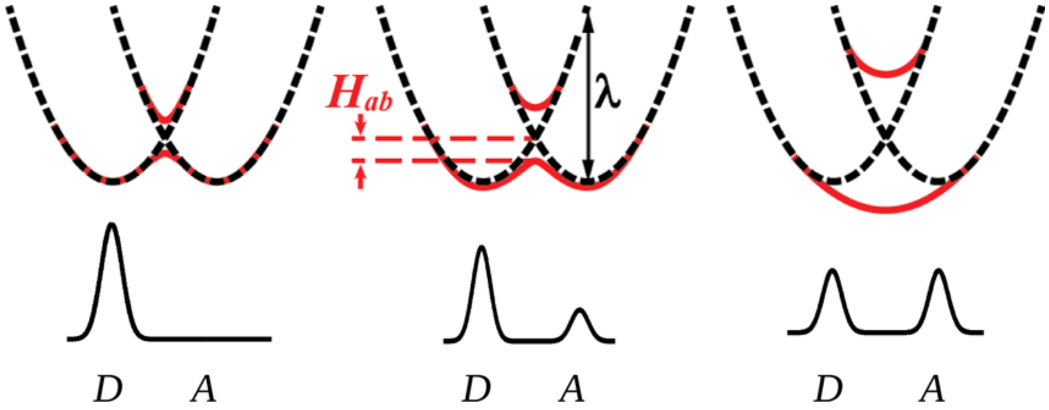

large barrier
localised states

small barrier
slightly
delocalised states

no barrier
no localised states

Some words on the hopping model

adiabatic or non-adiabatic? neither

Are there even charge localised states?
No, due to low reorganisation energy and high H_{ab}

$$\Downarrow$$

Hopping models based on localised site-to-site rates only suitable as first approximation. Can yield a starting point for future investigations.

A better way to simulate charge transport

Direct propagation of a model Hamiltonian parametrised from ab-initio calculations

- A. Troisi J. Chem. Phys. **134** 034702 (2011)
- F. Gajdos, M. Dupuis, and J. Blumberger *in preparation*

Simple Example

Assume a time independent Hamiltonian.

→ no coupling between electron and nuclear motion
(not really correct, see above)

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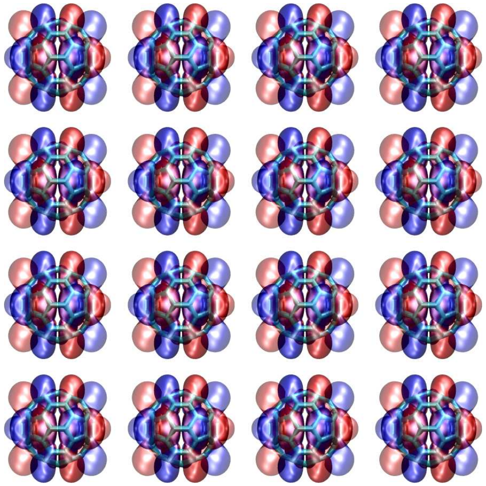

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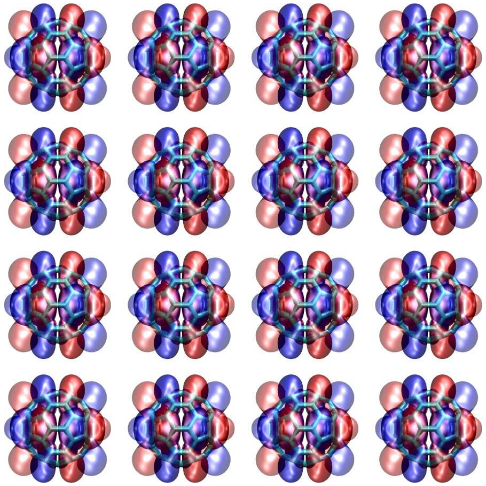

Model Hamiltonian:

off diagonal elements = H_{ab}
diagonal elements = Eigenenergies
of diabatic states

Simple Example

Solution to $\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t) = \mathbb{H}\Psi(\mathbf{r},t)$

- Choose initial state $\Psi_{\mathsf{I}}(\mathbf{r},t_0)$

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Simple Example

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- Solve $\mathbb{H}\Phi_i(\mathbf{r}) = \varepsilon_i\Phi_i(\mathbf{r})$ for time independent eigenvalues ε_i and eigenfunctions $\Phi_i(\mathbf{r})$
- Numerically propagate $\Psi_{\mathsf{I}}(\mathbf{r},t_0)$ for a time t:
  $\Psi(\mathbf{r},t) = \sum_i \left\langle \Phi_i(\mathbf{r}) | \Psi_{\mathsf{I}}(\mathbf{r},t_0)\right\rangle e^{-\mathrm{i}\varepsilon_i(t-t_0)/\hbar}\Phi_i(\mathbf{r})$

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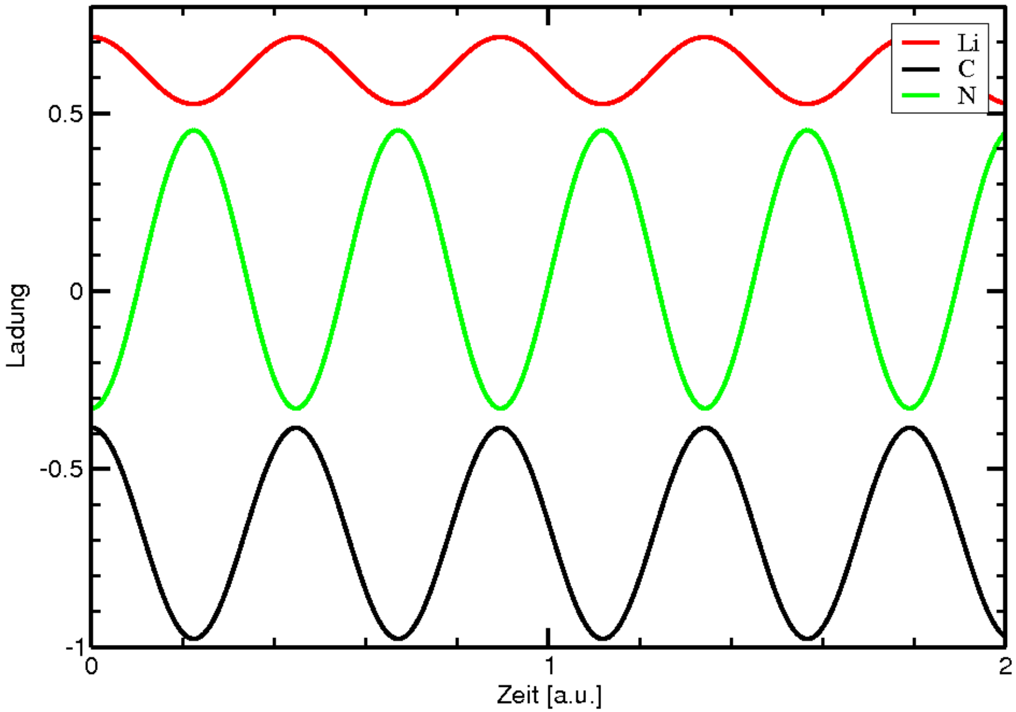
Work in progress for solar cells!

Simple Example

1D Example: Propagation of an excited core electron in LiCN

$Li—C\equiv N$



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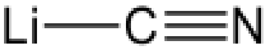
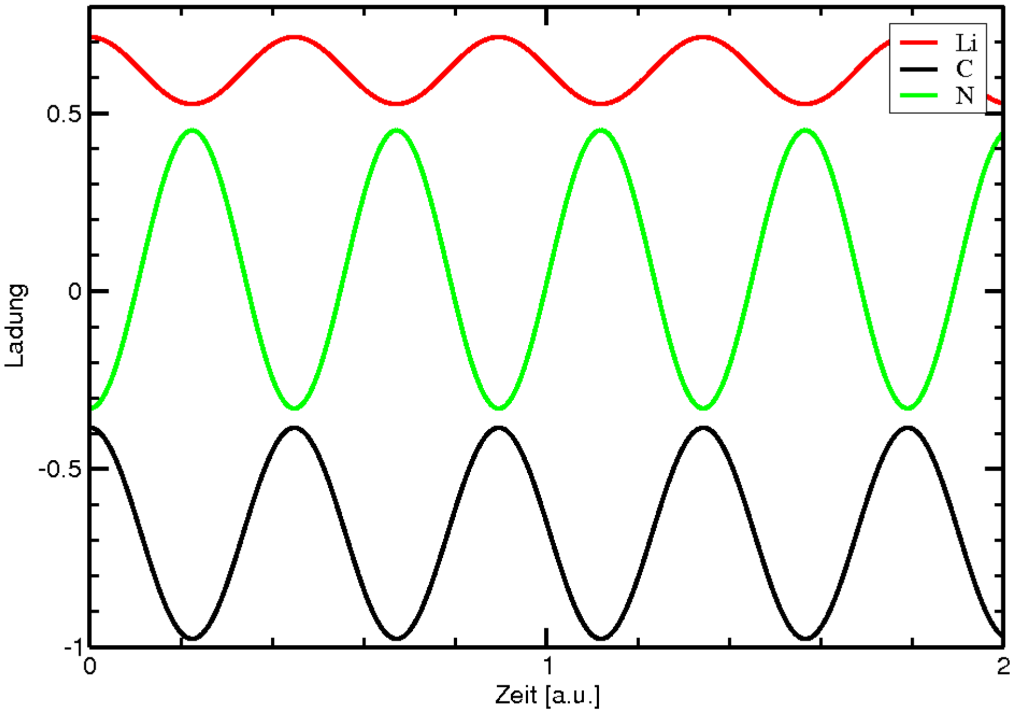
[1] M. Ludwig, internship report (2013)

Simple Example

1D Example: Propagation of an excited core electron in LiCN



Time dependent states
⇒ time series of atomic charges
⇒ can follow the movement of the electron through the molecule



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[1] M. Ludwig, internship report (2013)

Simple Example

What is missing (and some ideas how to proceed):

- Electric field → modify site energies
- Absorbing boundary conditions → imaginary site energies
- Movement of the atoms → force field or Born Oppenheimer DFT
- Coupling of electronic and nuclear motion
  → need non-adiabatic coupling element $\langle \psi_j(\mathbf{r},\mathbf{R}) | \nabla_{\mathbf{R}} \psi_i(\mathbf{r},\mathbf{R}) \rangle$