Lecture 4: Electronically excited states and theoretical spectroscopy; Polarizabilities, normal modes, vibrational spectra

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Guest Lecturers (e.g. use of Abinit, FHI-aims, USPEX)

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Outline

- Spectroscopy, electron-vibrational transitions
- Electronic spectroscopy modeling
- Wavefunction approaches and time-dependent DFT (TDDFT) for electronic spectra
- Nonlinear optical spectroscopies
- Vibrational spectroscopy modeling
- Nuclear magnetic resonance (NMR) spectroscopy

Spectroscopy (very incomplete list)

A MAJOR experimental tool to get information about the material:

- Electronic uv-vis spectroscopy: optical properties , electronic states;

- Time- and frequency- resolved nonlinear spectroscopies: dynamics of electronic system; rates, transport of energy and charges;

- Vibrational spectroscopy (Raman and IR): nuclei degrees of freedom and their dynamics

- Terahertz spectroscopy: dynamics of charges and low frequency vibrations;

- NMR (Nuclei Magnetic Resonance): structural information;

- EPR (Electron Paramagnetic Resonance) and ESR (Electron Spin Resonance) spectroscopy: spin dynamics in systems with unpaired electrons;

- PES (Photoemission Spectroscopy), also known as photoelectron spectroscopy: binding of electrons to material;

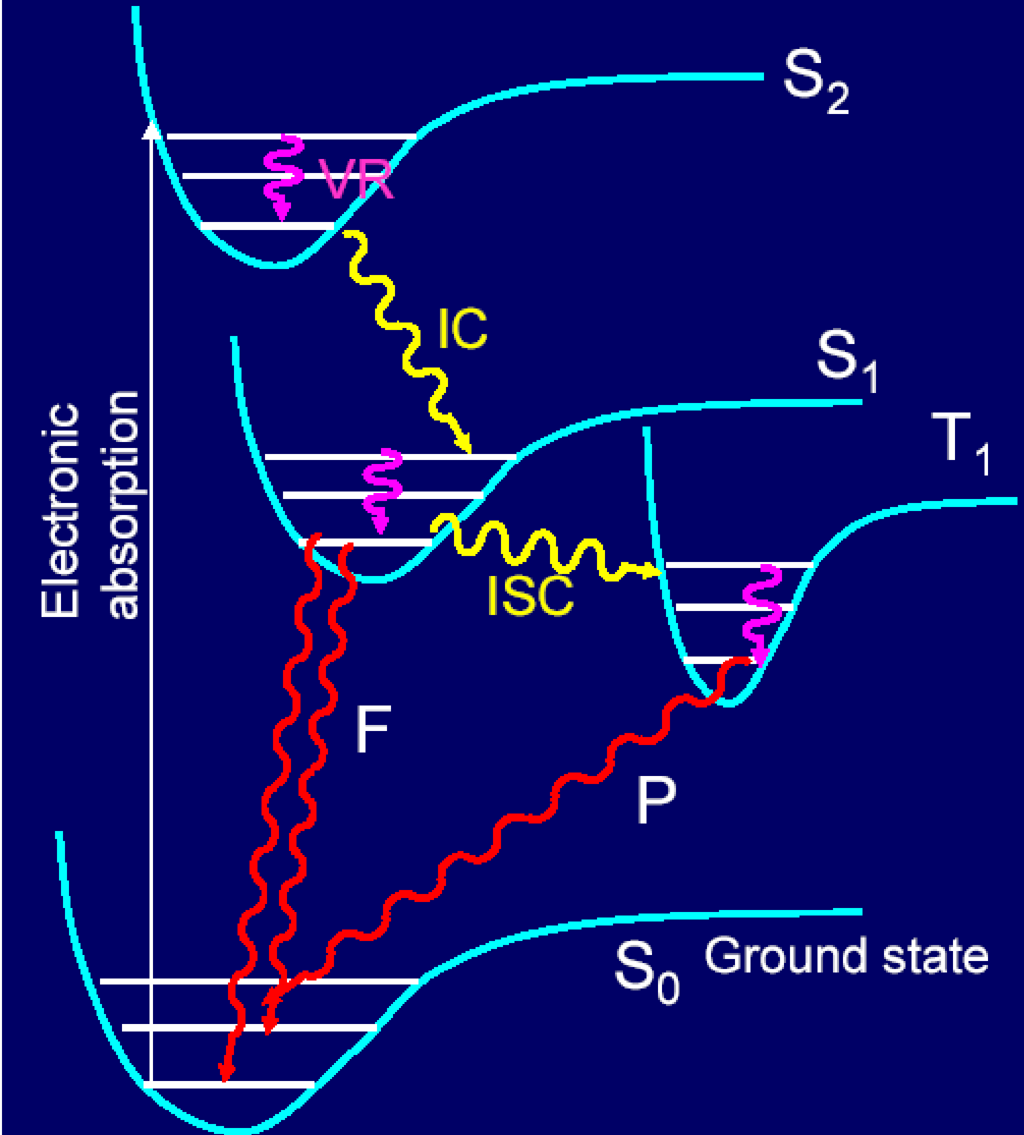
- XPS (X-ray photoelectron spectroscopy): elemental analysis of surface composition;

- STS (Scanning Tunneling Spectroscopy): density of electrons in a sample as a function of their energy;

- Etc.

Today we will deal with uv-vis absorption and emission spectroscopies – one of the standard experimental tools to characterize excited electronic state of various materials

Properties of Absorption and Emission

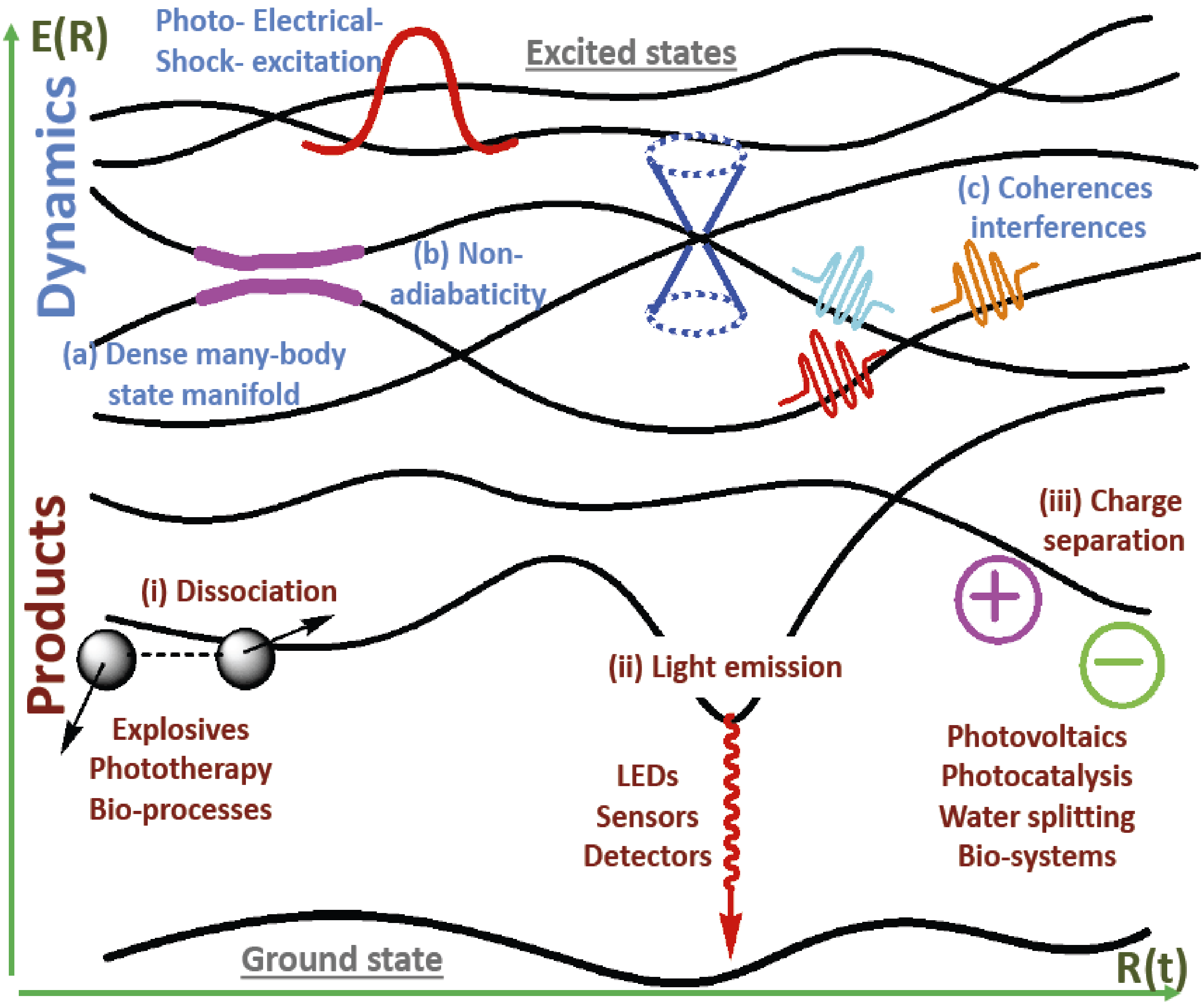


Absorption starts from the lowest vibrational level of the ground state

Fluorescence is red shifted (called Stokes shift) and is independent of excitation wavelength

The lifetime of phosphorescence is much longer than that of fluorescence

Photoinduced dynamics



Excited state relaxation timescales:

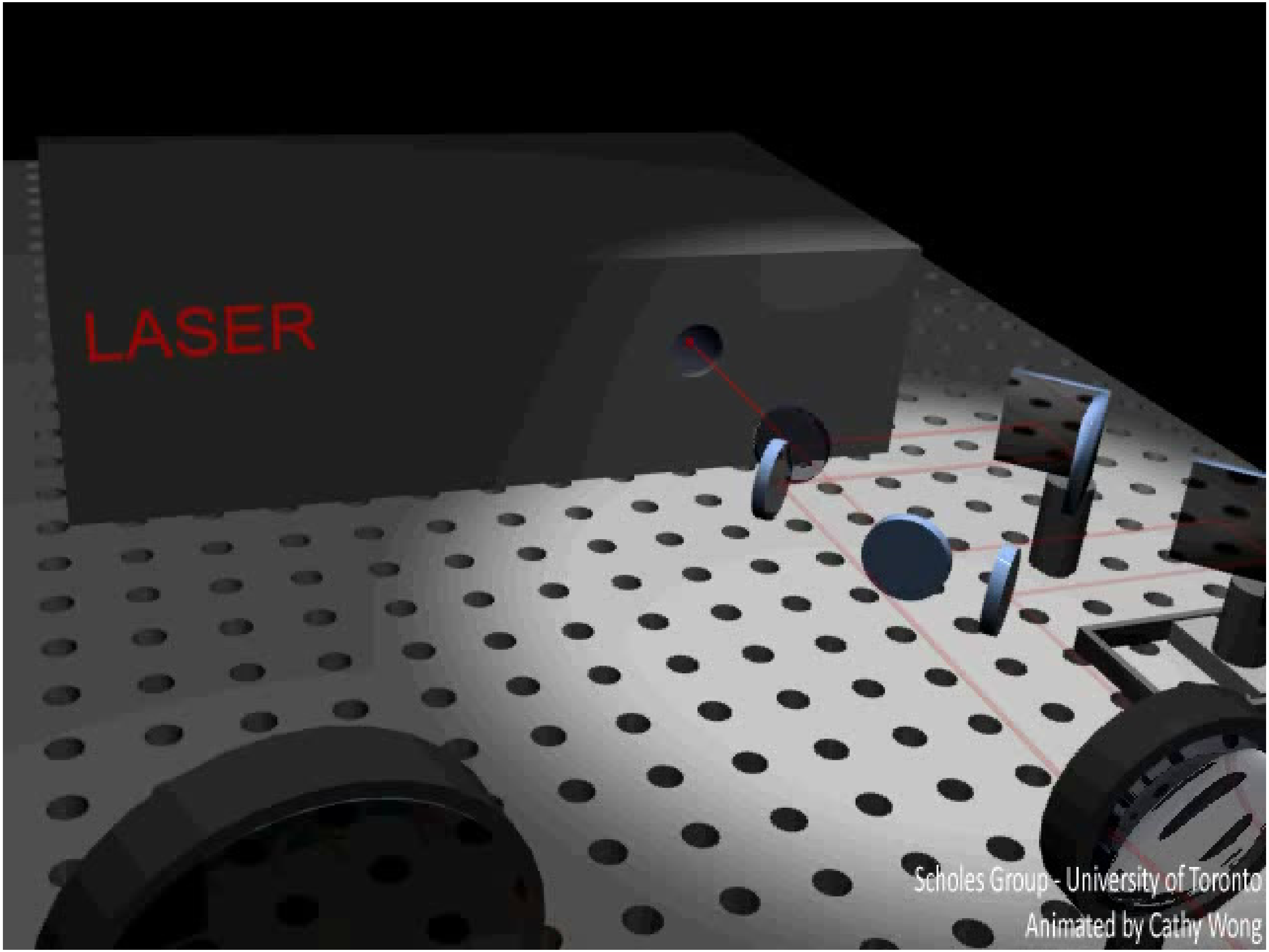
Phosphorescence decay
~ 1 ms

☐ Fluorescent decay
~ 1 ns

☐ Intraband relaxation
~ 10 ps

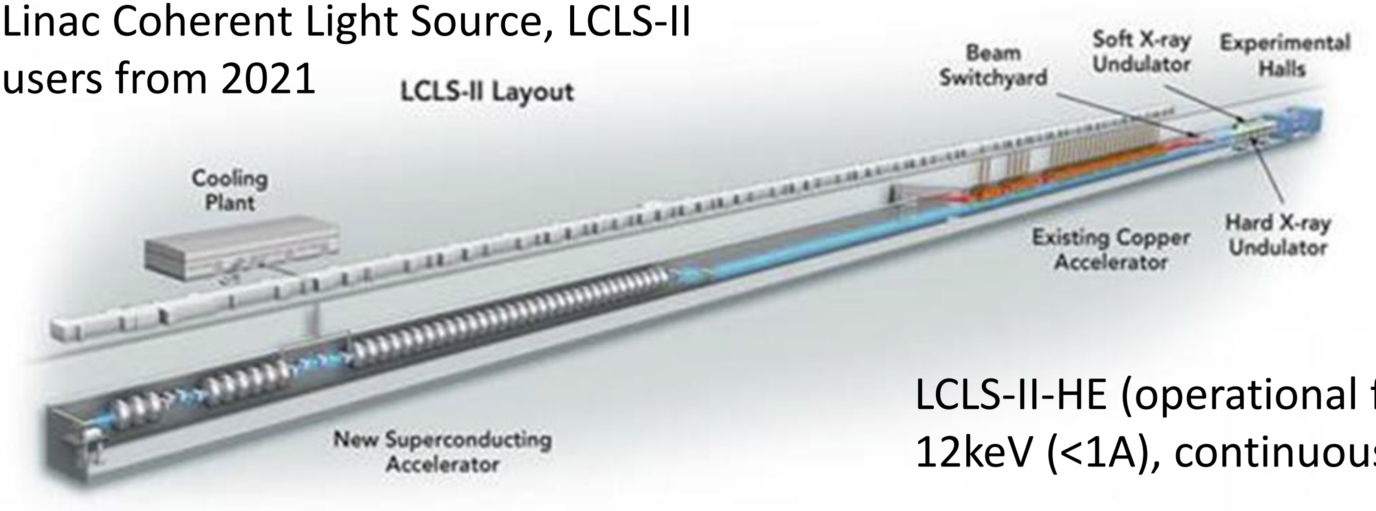
☐ Level crossing
~ 100 fs

Probing time & energy: spectroscopy



Probing time and space: X-Ray lasers

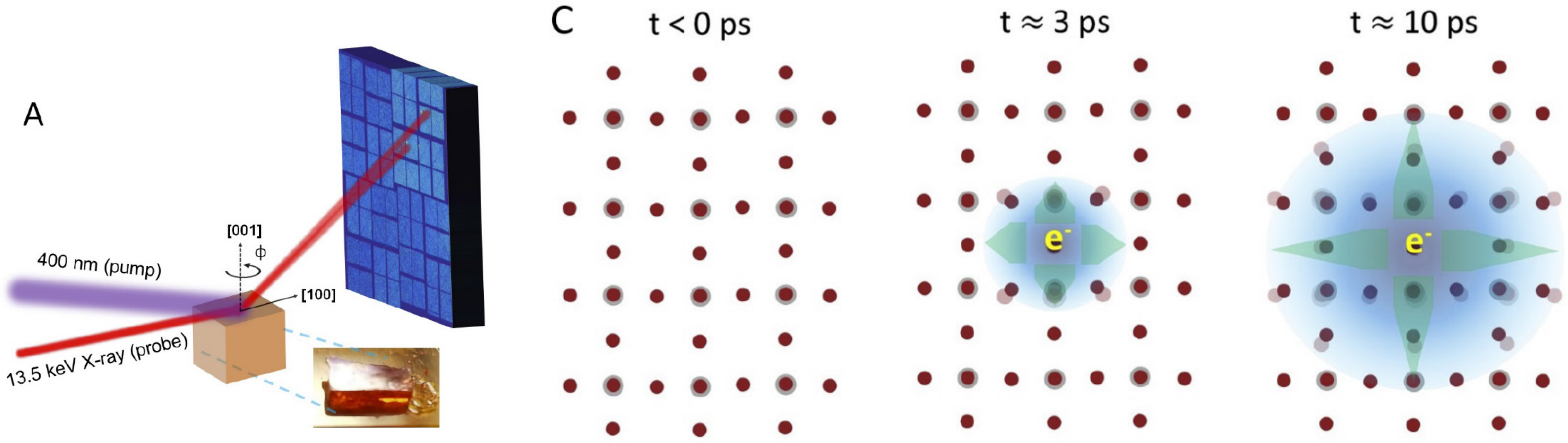
Linac Coherent Light Source, LCLS-II users from 2021



X-ray wavelengths extend down to the atomic scale, while x-ray pulse durations now lie in the femtosecond range.

LCLS-II-HE (operational from 2024): beyond 12keV (<1A), continuous pulse train (1 MHz).

Visualization of polaronic effects in halide perovskites



B. Guzelturk, T. Winkler, T. Van de Goor, M. D. Smith, S. A. Bourelle, S. Feldmann, M. Trigo, S. Teitelbaum, H-G. Steinruck, G. A. de la Pena, R. Alonso-Mori, D. Zhu, T. Sato, H. I. Karunadasa, M. F. Toney, F. Deschler, A. M. Lindenberg, Nature Materials (2020, in press)

Our toolbox

- Our material is composed from nuclei and electrons bound by Coulomb interactions
- Separate electronic (fast) from nuclei (slow) motion (adiabatic or Born-Oppenheimer approximation)
- Electronically excited state: any solution of the Schrodinger equation below but higher than the lowest energy solution (ground state)
- Solve the Schrodinger equation for molecular electronic Hamiltonian:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{iA}\frac{Z_A}{r_{iA}} + \sum_{i>j}\frac{1}{r_{ij}}\right]\psi_e(\mathbf{r};\mathbf{R}) = E_e\psi_e(\mathbf{r};\mathbf{R})$$

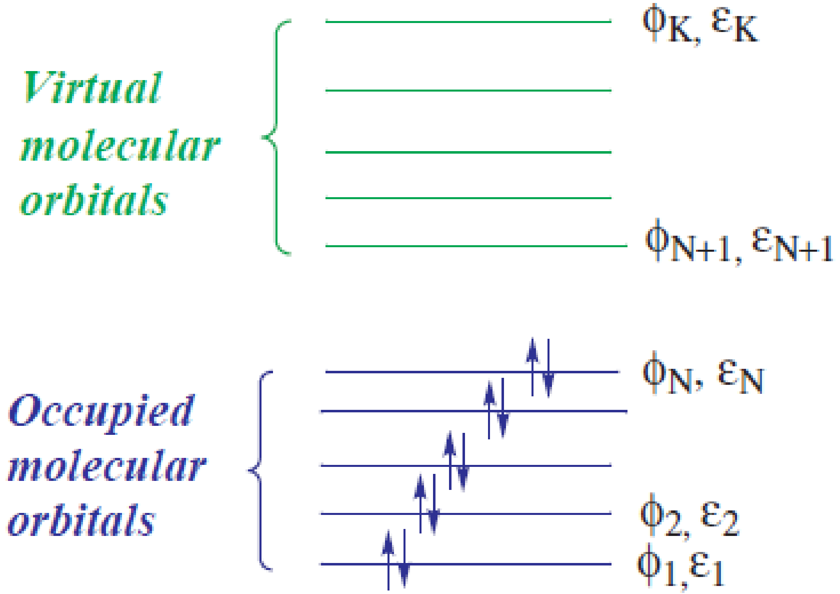
Method	*Hamiltonian*	*Wavefunction*	*Cost*
Ab initio *(e.g. HF, CAS-CI, CC-EOM)*	*Exact*	*Approximate* *(All electronic correlations)*	*Large* *(~10 atoms)*
Density Functional *(e.g. DFT, TDDFT)*	*Approximate, F(ρ),* *(All electronic correlations)*	*Fixed* *(Kohn-Sham system, mean field)*	*Significant* *(~100 atoms)*
Semiempirical *(e.g. AM1, MNDO, INDO/S)*	*Approximate,* *(Some electronic correlations)*	*Approximate* *(Some electronic correlations)*	*Low* *(~1000 atoms)*
Tight-binding *(e.g. Huckel, Frenkel, SSH)*	*Approximate,* *(Min electronic correlations)*	*Approximate* *(Usually uncorrelated)*	*Low* *(~10,000 atoms)*

Hartree-Fock procedure

For simplicity, assume an even number of electrons (closed shell)

Looking for a solution of electronic problem, $H_e\Psi = E\Psi$ where the wavefunction is a single Slater determinant $\Psi = |\phi_1 \dots \phi_N\rangle$ built on the (unknown) molecular orbitals

$$\phi_i(\mathbf{r}) = \sum_j^K C_{ij}\psi_j(\mathbf{r})$$



Ground state one-electron density matrix

$$\bar{\rho}_{nm} = 2\sum_a^{occ} C_{na}C^{\star}_{ma}$$

The Fock operator

$$F(\bar{\rho})_{nm} = t_{nm} + V(\bar{\rho})_{nm}$$

The Coulomb operator (V or G ~2J-K)

$$V(\bar{\rho})_{mn} = \sum_{k,l}^K \bar{\rho}_{kl}[\langle mk|nl\rangle - \frac{1}{2}\langle mn|kl\rangle]$$

The eigenvalue problem (secular equation)

$$FC = SC\varepsilon$$

Ground state energy $E = Tr(\bar{\rho}(F + t))$

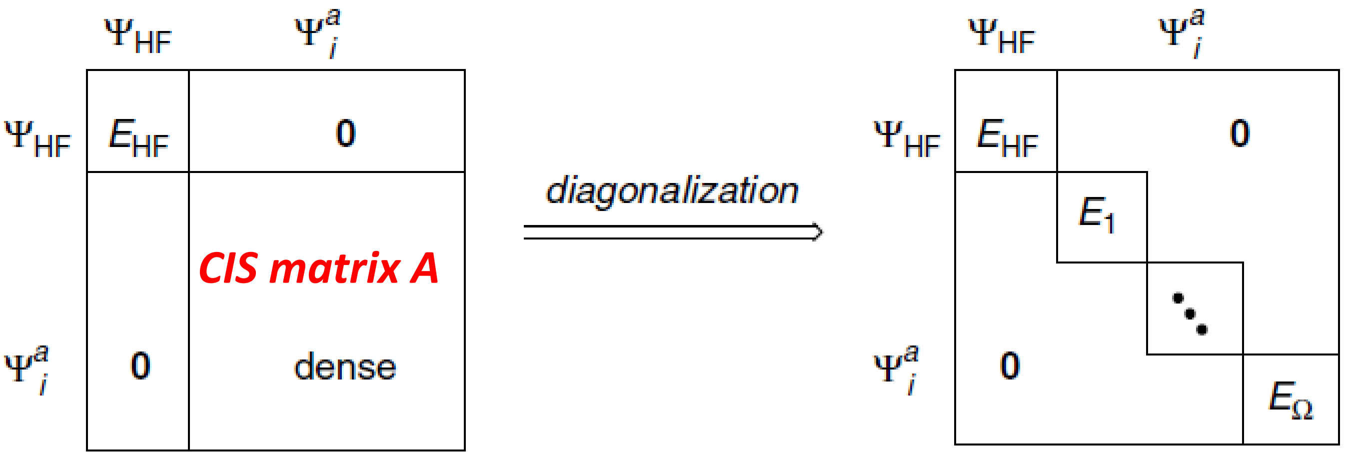
The total energy $E + \sum_{B>A}^M \frac{Z_A Z_B}{R_{AB}}$

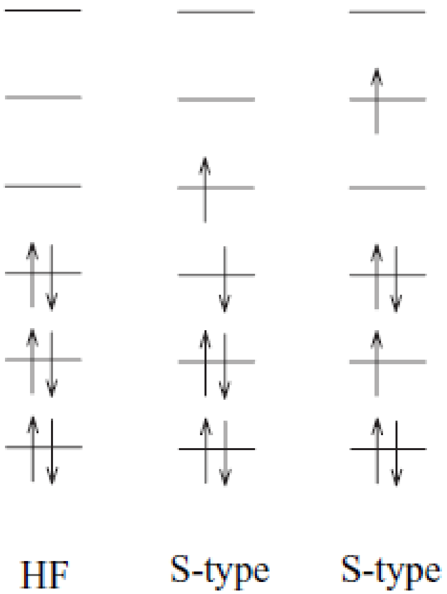
Nonlinear integro-differential equations, needs to be solved iteratively to achieve self-consistency!

A basic approach CIS (or Tamm-Dancoff)

Build the wavefunction as a superposition of singly excited determinants (these are orthogonal to the HF reference state)

$$\Psi_k = \sum_i^{\text{occupied}} \sum_a^{\text{virtual}} c_{iak} \Psi_i^a$$

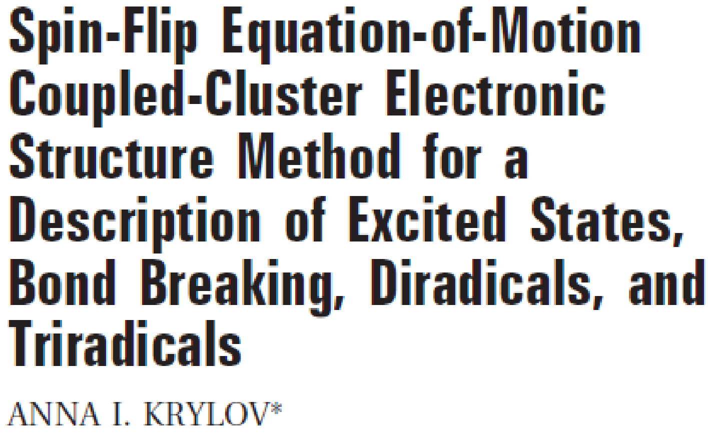




E_1, E_2, … are energies of excited states at the CIS level

Bottom line: relatively simple approach accounting for some electronic correlations (e.g., excitonic effects). Performance semiempirical CIS varies (ZINDO is usually accurate). Ab initio CIS is not accurate – transition energies are significantly shifted to the blue.

More accurate wavefunction approaches



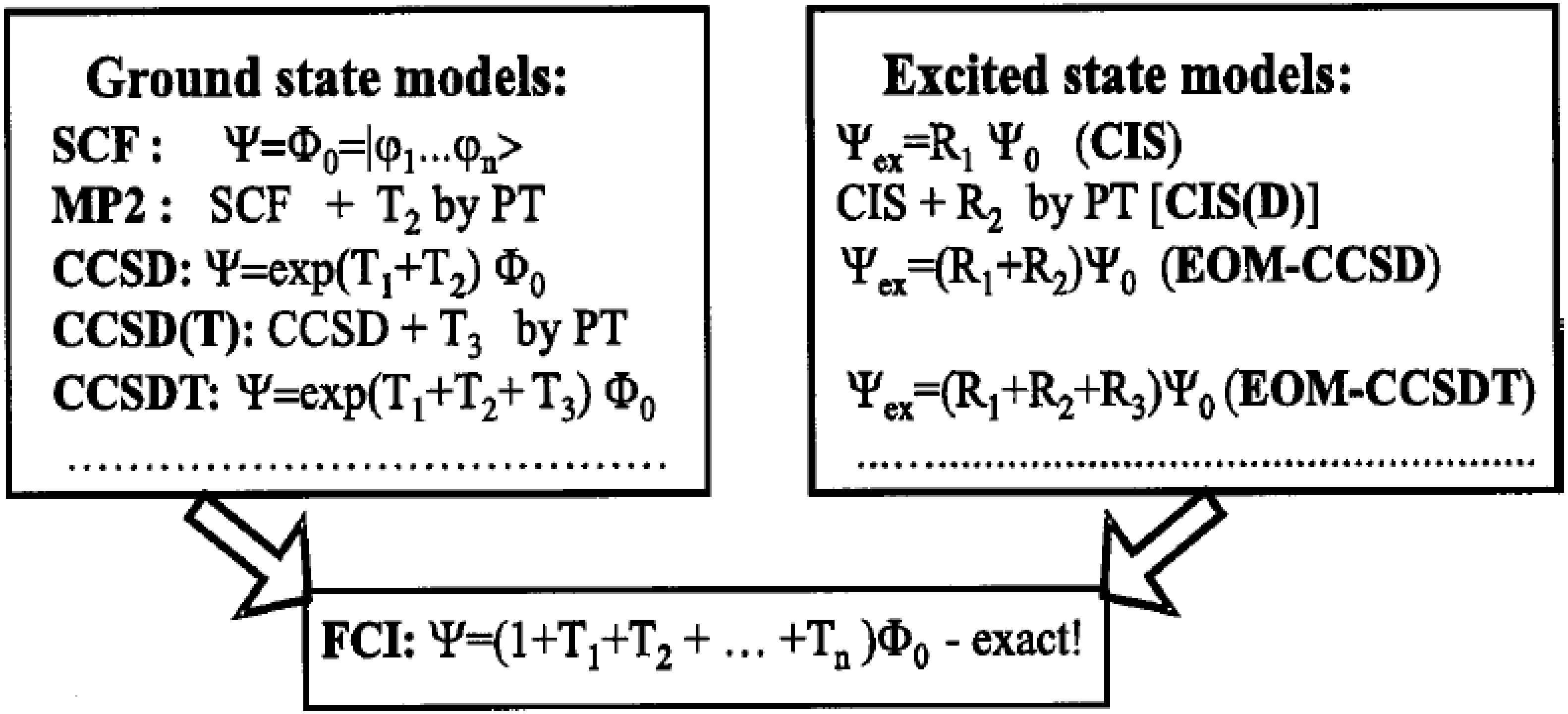
Spin-Flip Equation-of-Motion Coupled-Cluster Electronic Structure Method for a Description of Excited States, Bond Breaking, Diradicals, and Triradicals

ANNA I. KRYLOV*

VOL. 39, NO.

Higher order CI methods (e.g. CISD)

Coupled Cluster (CC) methods (e.g. EOM-CCSD)



Ground state models:

SCF : $\Psi=\Phi_0=|\varphi_1 \ldots \varphi_n>$

MP2 : SCF + T_2 by PT

CCSD: $\Psi=\exp(T_1+T_2)\,\Phi_0$

CCSD(T): CCSD + T_3 by PT

CCSDT: $\Psi=\exp(T_1+T_2+T_3)\,\Phi_0$

……

Excited state models:

$\Psi_{ex}=R_1\,\Psi_0$ (CIS)

CIS + R_2 by PT [CIS(D)]

$\Psi_{ex}=(R_1+R_2)\Psi_0$ (EOM-CCSD)

$\Psi_{ex}=(R_1+R_2+R_3)\Psi_0$ (EOM-CCSDT)

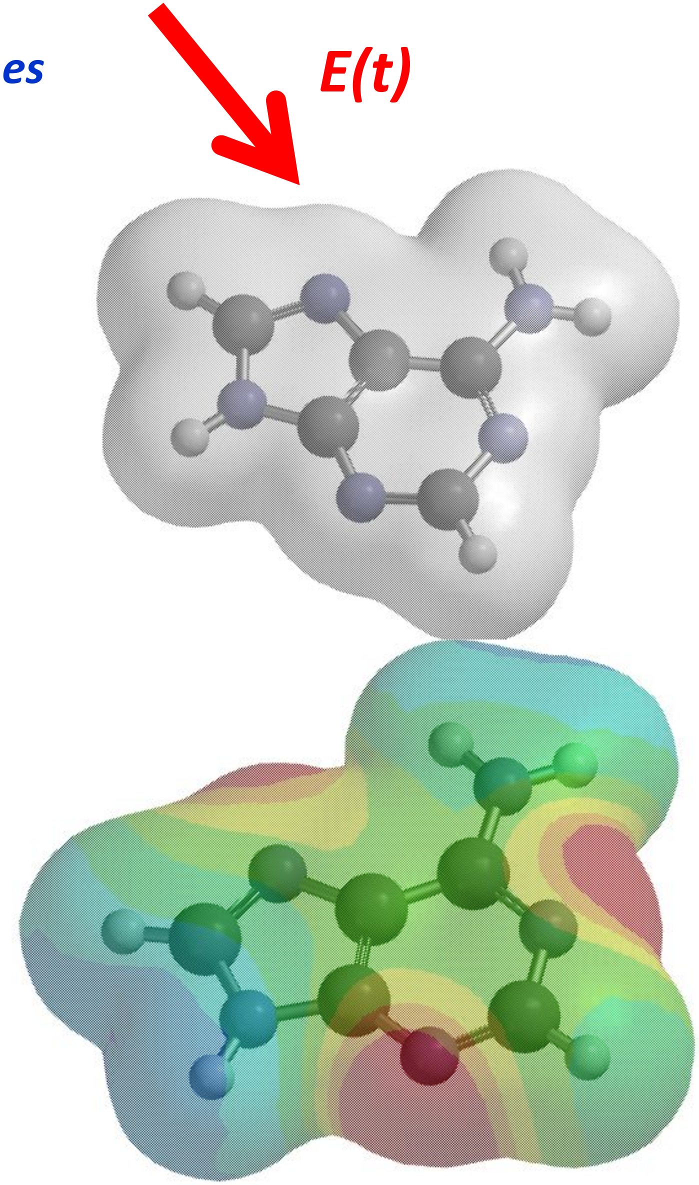
……

FCI: $\Psi=(1+T_1+T_2+\ldots+T_n)\Phi_0$ - exact!

Time-dependent methods

From HF reference state: time-dependent Hartree-Fock (TDHF) or Random Phase Approximation (RPA), sometimes approximated by CIS or Tamm-Dancoff approach

From DFT Kohn-Sham reference state: time-dependent Density Functional Theory (TDDFT), sometimes approximated by Tamm-Dancoff approach



General idea: introduce a weak perturbation (time-dependent electric field) and write equation of motion for a single-electron density matrix (Hamilton-Liouville's form):

$$i\frac{d\rho}{dt} = \{H_T, \rho\}$$

- Due to field the density will be oscillating;
- Excited electronic states will appear as resonant frequencies of these oscillations, i.e. peaks in the Fourier transform of the long trajectory;
- Beside time domain (time-dependent trajectories), excited state properties can be found directly in the frequency-domain by diagonalizing a specific matrix (operator), e.g., CIS matrix.

TDDFT is based on Runge-Gross Theorem:

Time-dependent charge density and density matrix are the main variables:

$$n(\mathbf{r},t) = \rho(\mathbf{r},\mathbf{r},t) \qquad \rho(\mathbf{r},\mathbf{r}',t) = \sum_p^N \psi_p(\mathbf{r},t)\psi_p^*(\mathbf{r}',t)$$

For any system with Hamiltonian of form $H = \overset{\text{kinetic}}{T} + \underset{\text{e-e interaction}}{W} + \overset{\text{external potential}}{V_{ext}}$,

Runge & Gross (1984) proved the 1-1 mapping:

$$n(\mathbf{r}\ t) \xleftrightarrow{\Psi_0} V_{ext}(r\ t)$$

- For a given initial-state ψ_0, the time-evolving one-body density $n(\mathbf{r}\ t)$ tells you *everything* about the time-evolving interacting electronic system, *exactly*.

This follows from :

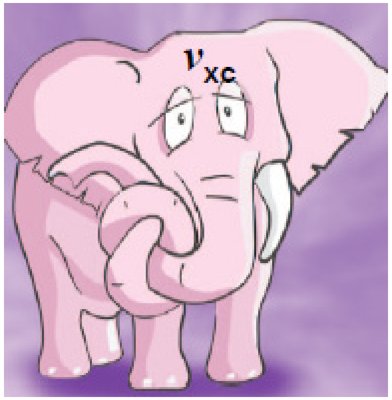
Ψ_0, $n(r,t)$ → unique $V_{ext}(r,t)$ → $H(t)$ → $\Psi(t)$ → all observables

Formal definitions of quantities:

The total potential for electrons: $v^{eff}(\mathbf{r},t) = \mathcal{P}(\mathbf{r},t) + v^{ext}(\mathbf{r}), + v^{cl}(\mathbf{r},t) + v^{xc}(\mathbf{r},t)$

Time-dependent perturbation: $\mathcal{P}_{ij\sigma}(t) = -\boldsymbol{\mathcal{E}}(t)\cdot\boldsymbol{\mu}_{ij\sigma} = -\sum_{s=x,y,z}\mathcal{E}^{(s)}(t)\mu_{ij\sigma}^{(s)}$

Dipole matrix: $\mu_{ij\sigma}^{(s)} = \int d\mathbf{r}\chi_{i\sigma}^{*}(\mathbf{r})\mathbf{r}^{(s)}\chi_{j\sigma}(\mathbf{r})$



Electron-nuclei interactions: $v^{ext}(\mathbf{r}) = \sum_{\alpha}\frac{-Z_\alpha}{|\mathbf{R}_\alpha - \mathbf{r}|}$

Electron-electron interactions: $v^{cl}(\mathbf{r},t) = \int\frac{n(\mathbf{r}',t)}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$

Definition of time-dependent exchange-correlation potential as a functional derivative of the exchange-correlation action

$$v^{xc}(\mathbf{r},t) = \frac{\delta A^{xc}[n]}{\delta n(\mathbf{r},t)}$$

The main 'practical' TDDFT approximation – derivative is 'local' in time (forget the history) – so-called adiabatic approximation

$$v^{xc}(\mathbf{r},t) \approx \frac{\delta E^{xc}[n_t]}{\delta n_t(\mathbf{r},t)}$$

Version 1: time-dependent propagation

Consider an *N*-electron system, starting from a stationary state. The stationary point is defined by a solution of the static Kohn-Sham equations (P(r, t) = 0)

$$\left[-\frac{1}{2}\nabla^2 + v^{ext}(\mathbf{r}) + v^{cl}[\bar{n}](\mathbf{r}) + v^{xc}[\bar{n}](\mathbf{r})\right]\varphi_p(\mathbf{r}) = \varepsilon_p\varphi_p(\mathbf{r})$$

$$\bar{n}(\mathbf{r}) = \bar{\rho}(\mathbf{r},\mathbf{r}) = \textstyle\sum_p^N |\varphi_p(\mathbf{r})|^2$$

The *N* static KS orbitals are taken as initial orbitals and will be propagated in time:

$$i\frac{\partial\psi_p(\mathbf{r},t)}{\partial t} = \left[-\frac{1}{2}\nabla^2 + v^{eff}(\mathbf{r},t)\right]\psi_p(\mathbf{r},t)$$

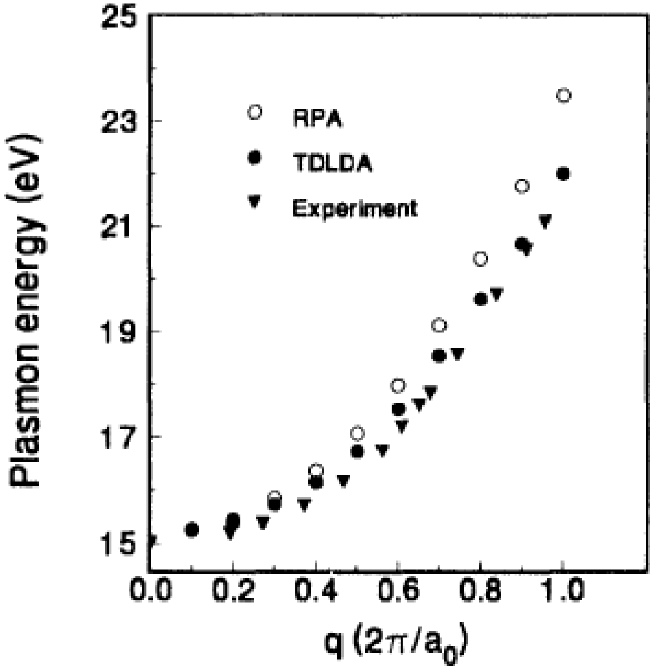
Time-dependent density: $n(\mathbf{r},t) = \sum_{j=1}^{N} |\phi_j(\mathbf{r},t)|^2$

Time-dependent energy: $E[\bar{n}] = T[\bar{n}] + E^{ext}[\bar{n}] + E^{cl}[\bar{n}] + E^{xc}[\bar{n}]$

I.e., by propagating KS differential equations we have established time-dependent behavior of density and energy (as well as other observables).

Such scheme is well suited to description of periodic systems (evolution of electronic system under perturbation, such as electric field). Sometimes dubbed as Real-Time DFT (RT-DFT)

Example 1: TDDFT in solids, excitations in metals



Plasmon dispersion of Al

Quong and Eguiluz, PRL **70**, 3955 (1993

- ►RPA (i.e., Hartree) gives already reasonably good agreement
- ►ALDA agrees very well with exp.

In general, (optical) excitation processes in (simple) metals are very well described by TDDFT within ALDA.

Time-dependent Hartree already gives the dominant contribution, and f_{xc} typically gives some (minor) corrections.

This is also the case for 2DEGs in doped semiconductor heterostructures

Version 2: frequency domain calculations

So-called Casida approach (for TDDFT) or RPA equations (for TDHF).

Density matrix is time-dependent under perturbation $\rho = \bar{\rho} + \delta\rho(t)$

Its time-evolution $i\frac{d\delta\rho}{dt} = [F(\rho), \rho] + [\mathcal{P}(t), \rho]$ Stationary point $[F(\bar{\rho}), \bar{\rho}] = 0$

Fock or KS operator $F_{ij\sigma}(\rho) = t_{ij\sigma} + V_{ij\sigma}(\rho) + v^{xc}_{ij\sigma}(\rho)$

Coulomb operator

$$V_{ij\sigma}(\rho) = \sum_{kl\sigma'}((ij\sigma|kl\sigma')\rho_{kl\sigma'} - c_x(ik\sigma|jl\sigma)\rho_{kl\sigma}\delta_{\sigma\sigma'})$$

Exchange-correlation operator: should be expanded to the first order in $\delta\rho$(t)

$$v^{xc}(\rho) = v^{(0)} + v^{(1)}(\delta\rho) \qquad v^{(1)}_{ij\sigma}(\delta\rho) = \sum_{kl\sigma'} f_{ij\sigma,kl\sigma'}\delta\rho_{kl\sigma'}$$

$$v^{(0)}_{\sigma}(\mathbf{r}) = \frac{\delta E^{xc}}{\delta n_\sigma(\mathbf{r})} \qquad f_{\sigma\sigma'}(\mathbf{r},\mathbf{r}') = \frac{\delta^2 E^{xc}}{\delta n_\sigma(\mathbf{r})\delta n_{\sigma'}(\mathbf{r}')}$$

Note appearance of the next derivative of exchange-correlation functional E^{xc}: the above equation of motion for density matrix is written in the first order perturbation in $\delta\rho$(t) – therefore TDHF or TDDFT are called linear response theories

Version 2: frequency domain calculations

It is instructive to introduce a 'tetradic' Liouville space (density matrices are matrices in the Hilbert space but vectors in the Liouville space)

$$\rho = \bar{\rho} + \xi(t)$$

The time-evolution of a vector ξ(t) is then

$$i\frac{\partial \xi}{\partial t} - L\xi = -\boldsymbol{\mathcal{E}}(t) \cdot [\boldsymbol{\mu}, \bar{\rho}]$$

Formally, it is an equation of motion of the coupled system of oscillators driven by perturbation! How many oscillators? – the number of components in the density matrix ξ(t)

Solving if in frequency-domain means diagonalization of *L* to find the eigenmodes of oscillators

So-called RPA eigenproblem of size N(N-K)/2, N-electrons, K-basis functions

$$\begin{pmatrix} A & B \\ -B & -A \end{pmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \Omega \begin{bmatrix} X \\ Y \end{bmatrix}$$

Note here A is exactly the CIS matrix

$$A_{ia\sigma,jb\sigma'} = (\varepsilon_{a\sigma} - \varepsilon_{i\sigma})\delta_{ij}\delta_{ab}\delta_{\sigma\sigma'} + (ia\sigma|jb\sigma') + f_{ia\sigma,jb\sigma'} - c_x(ab\sigma|ij\sigma)\delta_{\sigma\sigma'},$$

$$B_{ia\sigma,jb\sigma'} = (ia\sigma|jb\sigma') + f_{ia\sigma,jb\sigma'} - c_x(ja\sigma|ib\sigma)\delta_{\sigma\sigma'},$$

Direct diagonalization (brute force approach) is very expensive (~N^6 cost). Fortunately Krylov subspace numerical approaches reduce it to ~N^3.

Krylov space algorithms – a shortcut!

If we will diagonalize the RPA/CIS approaches directly, we will get N(N-K) oscillators representing excited electronic molecular states, spanning frequency range from IR/visible to UV to X-ray. Usually we do not need so many of those -10…100 is a specific energy range will suffice. These can be obtained at a reduced numerical cost!

$$L\xi_\nu = \Omega_\nu \xi_\nu$$

All we need to know how superoperator *L* acts on an arbitrary vector (i.e. density matrix). The result does carry information about eigenspectrum of *L*!

Here we are back matrix-matrix operations (products and commutators)

$$L\xi = [F(\bar{\rho}), \xi] + [\tilde{V}(\xi), \bar{\rho}] \qquad F(\rho) = \tilde{t} + \tilde{V}(\rho)$$

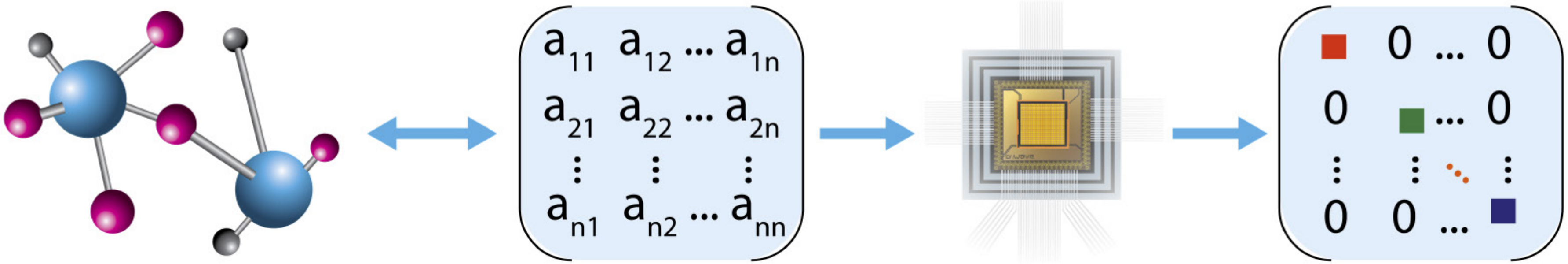
$$\tilde{t} = t + v^{(0)} \qquad \tilde{V}(\rho) = V(\rho) + v^{(1)}(\delta\rho)$$

Idea of Krylov-subspace approaches (Davidson, Lanczos, conjugated gradient, etc): Start with trial vector ξ, form sequence ***L***ξ, ***L²***ξ, ***L³***ξ, …, from this sequence evaluate partial eigenspectrum of ***L***

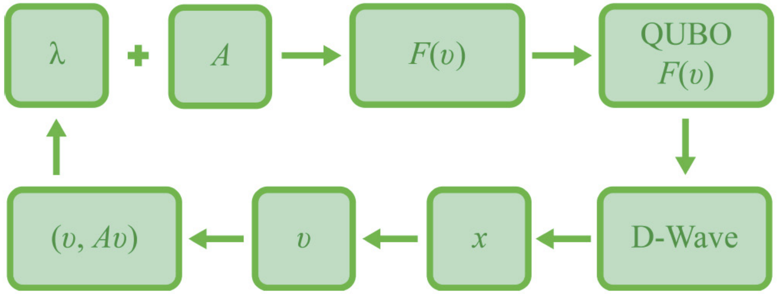
Bottom line: calculation of electronically excited states involves 2 steps

- ***Ground state calculations (Fock-matrix diagonalization, cost ~N³)*** $\quad FC = C\epsilon$
- ***Partial diagonalization of Liouville operator (cost ~N³)*** $\quad L\xi_\nu = \Omega_\nu \xi_\nu$

Excited states on a quantum computer



$R_A = (v, Av)/(v, v)$ Seeking solution to minimize Rayleigh-Ritz quotient



Loop for optimization of an objective function *F*

$F(v) = (v, Av) + \lambda \cdot (v, v)$ λ – search is fully automated

Quadratic Unconstrained Binary Optimization (QUBO) solves for ground state on D-wave $x_i \in \{0, 1\}$

Excited states are generated by shifting levels in the eigenspectrum $A' = A + S_0(v_0 \otimes v_0)$

Excited states of water at FCI/sto-3g level

Transition	T_{ref} [a]	T_{cl} [b]	T_{hw} [c]
$S_0 \rightarrow S_1$	303.056	300.563	302.125
$S_0 \rightarrow S_2$	369.233	373.585	379.837
$S_0 \rightarrow S_3$	441.058	437.217	444.802
$S_0 \rightarrow S_4$	590.407	606.617	612.352

Quantum-computer hardware is a nice 'toy', where we are re-learning the basic linear algebra from a new angle

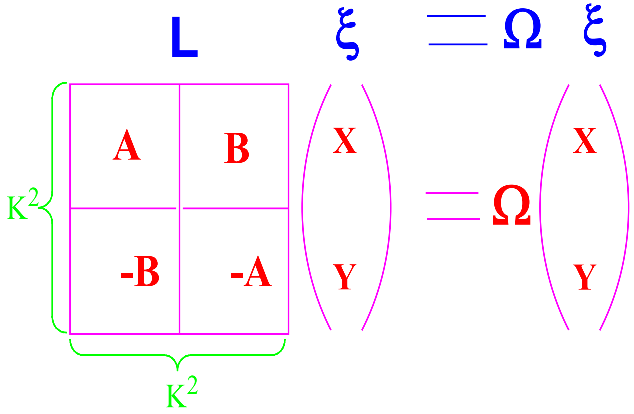
A. Teplukhin, B. K. Kendrick, S. Tretiak and P. A. Dub, Sci. Rep., (2020, in press)

Let summarize….

- ***TD equation of motion:***

$$i\frac{\partial \rho_{mn}(t)}{\partial t} = [F(\rho), \rho] - \mathcal{E}(t)[\mu, \rho]$$

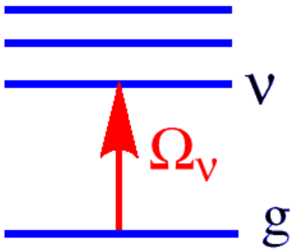
$$L\xi_\nu = \Omega_\nu \xi_\nu$$



A, X - CIS (particle-hole) part

- ***Electronic normal modes or transition densities***

$$(\xi_\nu)_{ij} = \langle \Psi_\nu | c_i^+ c_j | \Psi_g \rangle$$



- ***Krylov subspace algorithms (e.g. Davidson, Lanczos)***

- **Scaling of computational effort:**
  - ***Time*** **~N^3**
  - ***Memory*** **~N^2**

Cost/per excited state is smaller than SCF ground state effort

TDHF: Dirac, Pines, Bartlett, Schmitt-Rink, Jorgensen, McKoy, Fukotome ….

TDDFT: Runge, Gross, Casida, Perdew, Becke, Yang, Burke, Furche ….

What about spectroscopy?

If we will neglect vibronic effects, to compute absorption spectra one needs transition frequencies and transition densities. The latter can be used to calculate transition dipole moments and oscillator strengths related to the absorption of individual electronic states

Transition dipole moments

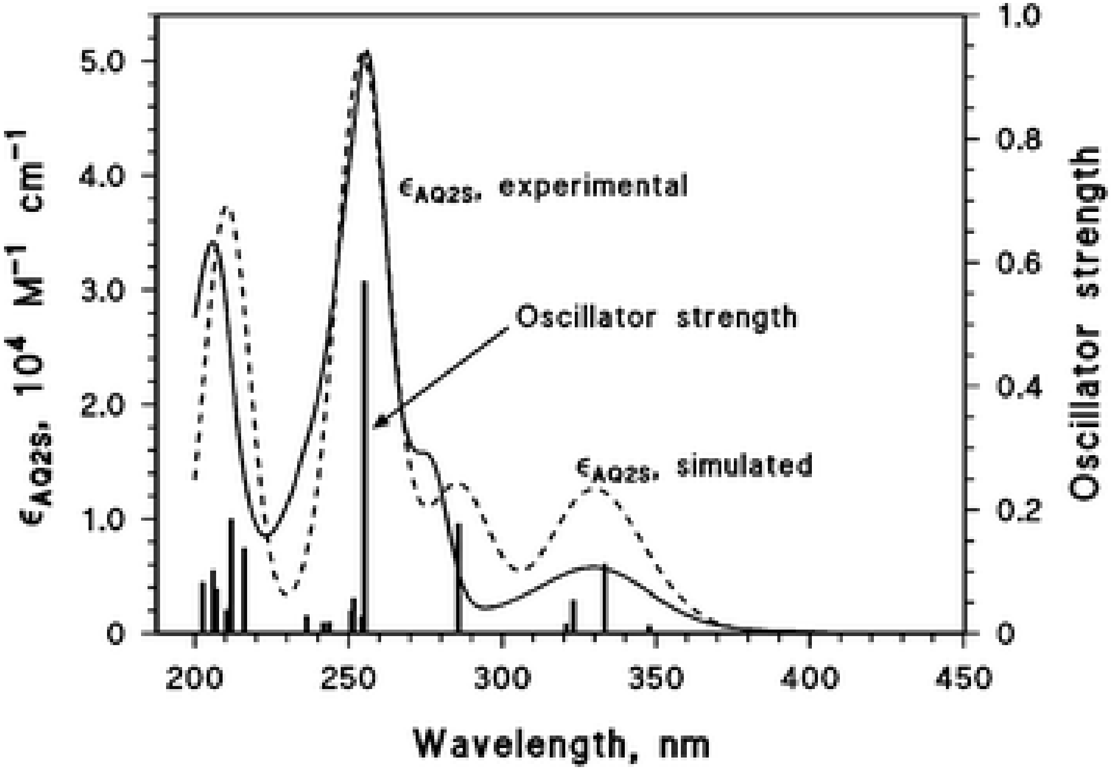
$$\boldsymbol{\mu}_\alpha = Tr(\boldsymbol{\mu}\xi_\alpha)$$

Oscillator strength:

$$f_\alpha \sim \frac{2}{3}\Omega_\alpha((\mu_x)^2_\alpha + (\mu_y)^2_\alpha + (\mu_z)^2_\alpha)$$

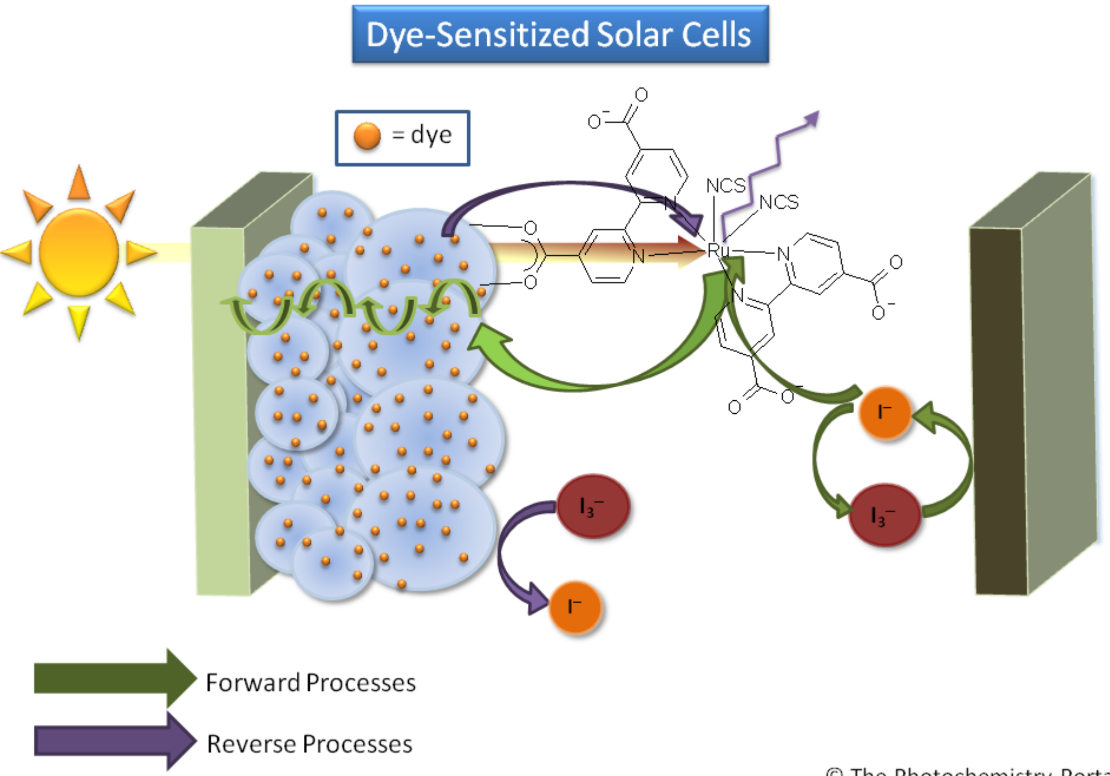
Approximation for calculated absorption profile using empirical broadening:

$$\alpha(\omega) = \sum_\nu \frac{2\Omega_\nu \mu_{g\nu}\mu^*_{g\nu}}{\Omega^2_\nu - (\omega + i\Gamma)^2}$$



A. Bedini et al., Photochem. Photobiol. Sci., 2012,**11**, 1445-1453

Practice 1: Organo-metallic compounds



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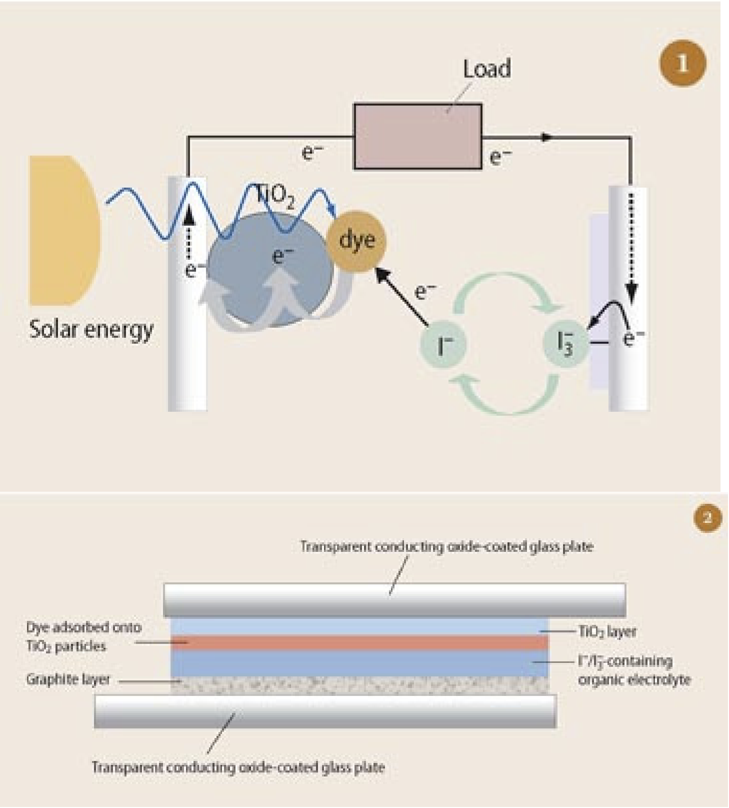


Forward and reverse electronic pathways in a dye-sensitized (Gratzel) solar cells

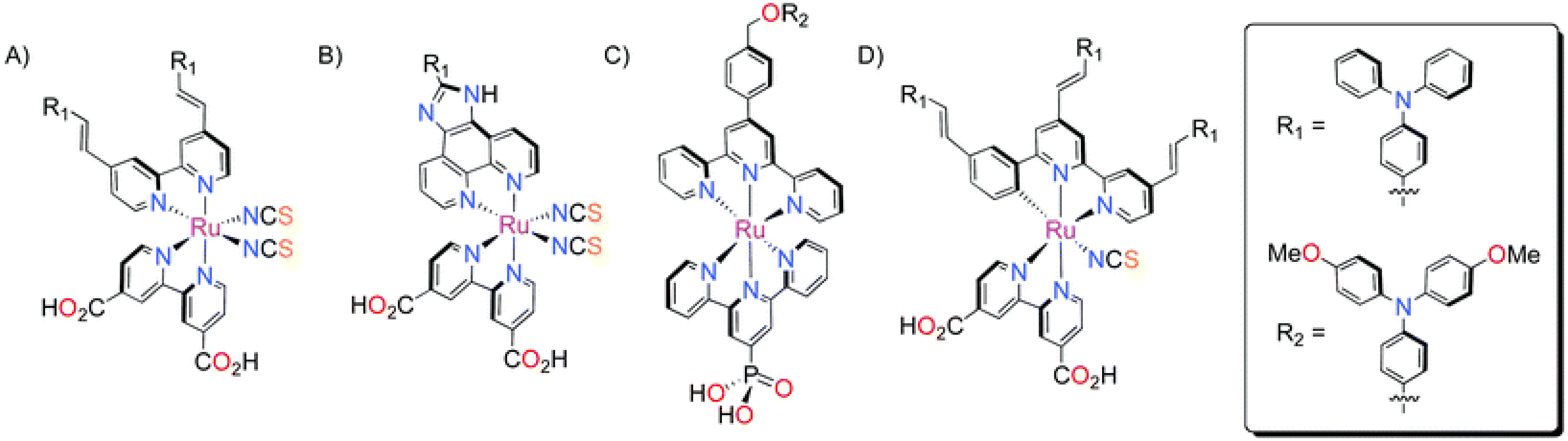
Synthesis of new optically active dyes is an important research area

Disadvantages:

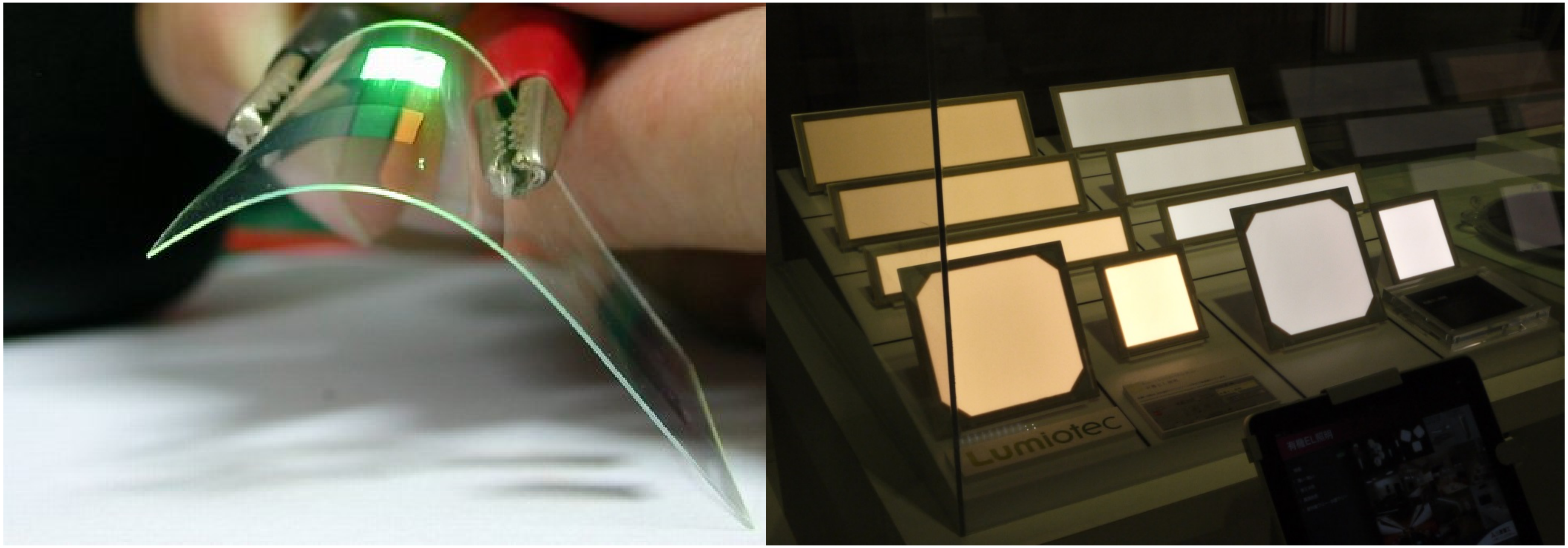
- ***Use of liquid electrolyte;***
- ***Ru is expensive;***
- ***Pt is expensive.***

Practice 1: Organo-metallic compounds

Experimentalist: I can make new Ru-based dyes. Can you provide some predictions about their uv-vis spectra and electronic states to guide my synthesis?



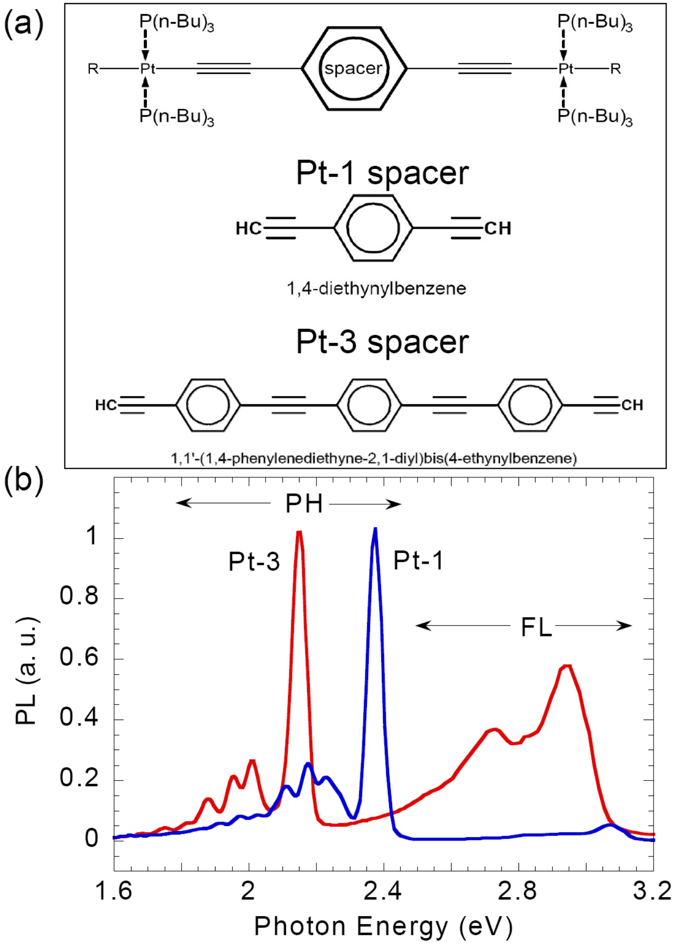
Case study 1: Intersystem crossings

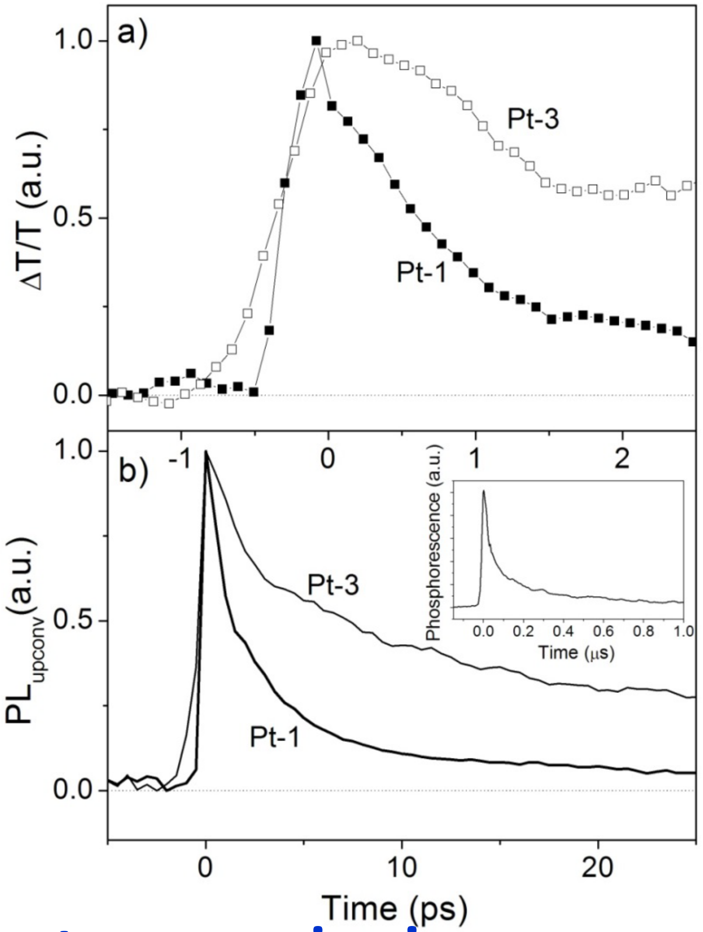


A flexible OLED device (left) and prototype OLED lighting panels

Problem: obtain broad band light emission (i.e. white light)
One solution: use both singlet (fluorescence) and triplet (phosphorescence) emission
Difficulty: need to arrange spin-orbit coupling to control singlet-triplet transfer rates(i.e. intersystem crossing) using heavy elements (e.g., metals)

Case study 1: π-conjugated polymers with tunable spin-orbit coupling: Pt-acetylene complexes



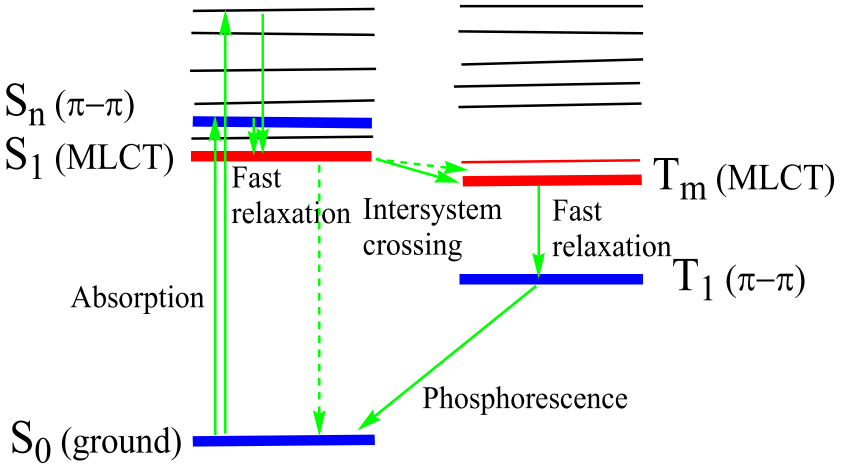


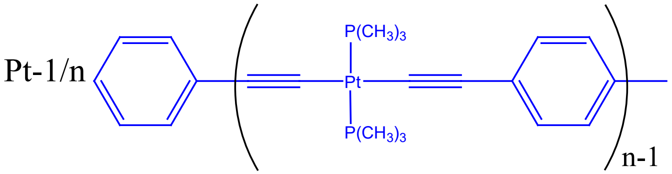
Experiment: S->T intersystem crossing is

~1ps in Pt-1 and ~6ps in Pt-3… Why???

C.-X. Sheng, S. Singh, A. Gambetta, T. Drori, M. Tong, S. Tretiak, Z. V. Vardeny Sci. Rep., 3 2653 (2013).

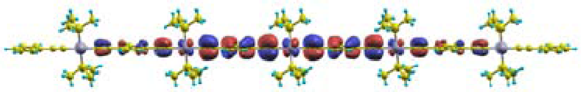
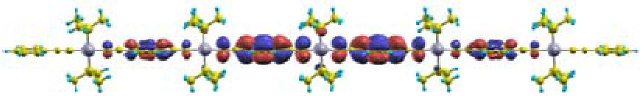
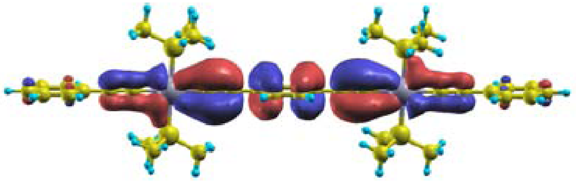
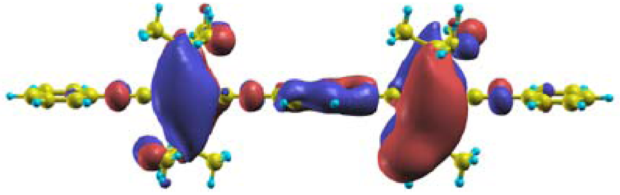
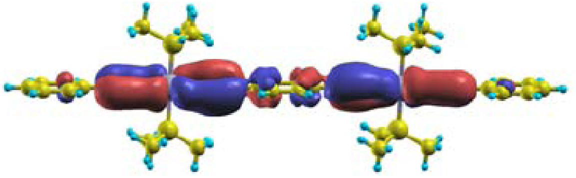
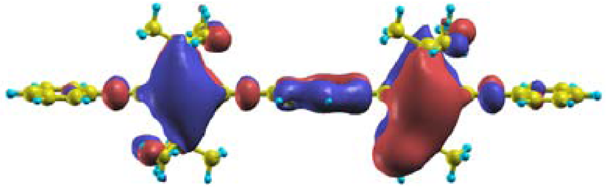
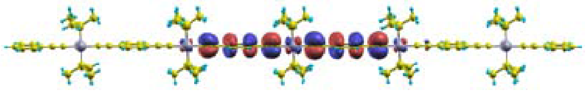
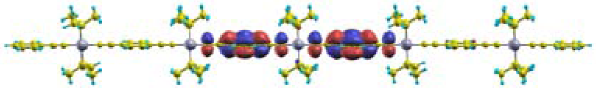
Case study 1: Pt-1 excited state structure



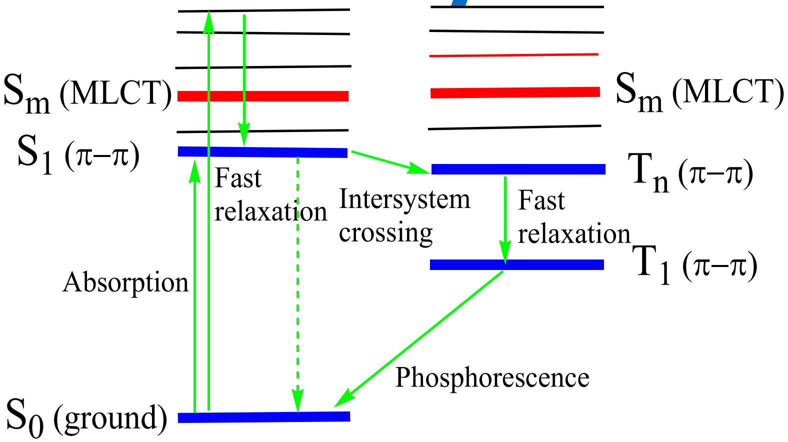


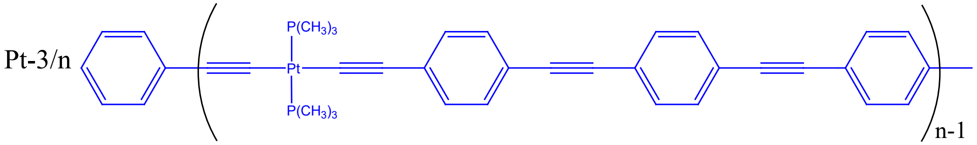
Ultrafast intersystem crossing goes through 'similar' S and T excited states of MLCT character!

C.-X. Sheng, S. Singh, A. Gambetta, T. Drori, M. Tong, S. Tretiak, Z. V. Vardeny Sci. Rep., 3 2653 (2013).

1) Photoabsorption to the allowed π–π state.		
2) Fast internal conversion within singlets to the lowest LMCT state.		
3) Intersystem crossing from LMCT singlet to LMCT triplet states.		
4) Fast internal conversion within triplets to the lowest π–π state.		

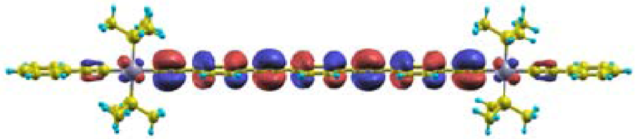
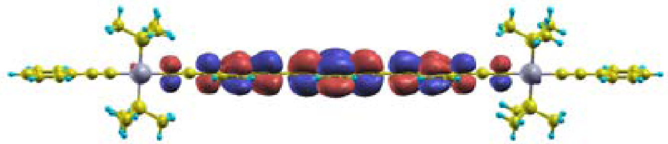
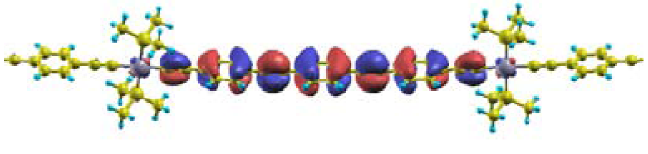
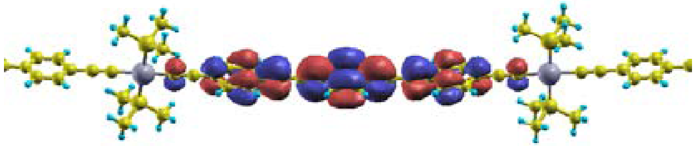
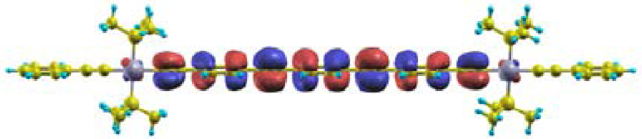
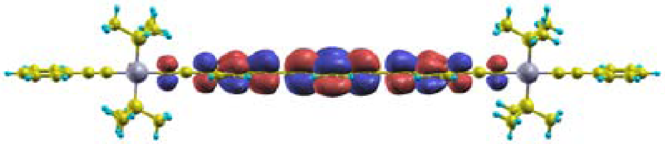
Case study 1: Pt-3 excited state structure





Intersystem crossing goes through π–π* excited states only (like in pristine polymer). The rate decreases from <1ps to 6 ps!

C.-X. Sheng, S. Singh, A. Gambetta, T. Drori, M. Tong, S. Tretiak, Z. V. Vardeny Sci. Rep., 3 2653 (2013).

1) Photoabsorption to the allowed π–π state.		
2) Intersystem crossing from π–π singlet to π–π triplet states.		
3) Fast internal conversion within π–π triplets to the lowest state.		

Calculations: TD-B3LYP/6-31G*(Pt-lanl2dz) // B3LYP/6-31G* (Pt-lanl2dz)

Discussion

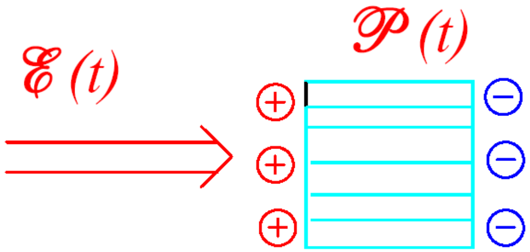
1. Why excited states obtained from CIS is a better approximation compared to monoelectronic excitations (e.g. HOMO-LUMO)?

2. Question to all: write on the chat, to which variable ‘time dependent’ expression is referred to in TD-DFT framework.

3. Give some examples of experimentally-relevant observables that can be evaluated after TD-DFT calculations of excited states.

4. *Why in molecular systems triplet states are much lower than singlet excited states? Why this is not the case for conventional semiconductors?

Linear and nonlinear optical responses



Optical polarizability

$$\mathcal{P} = \alpha\mathcal{E} + \beta\mathcal{E}^2 + \gamma\mathcal{E}^3 + \cdots$$

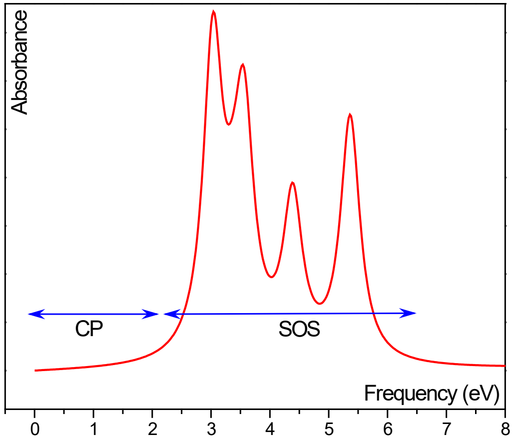
$$\mathcal{P}_i(\omega) = \mu_i^{(0)} + \boxed{\alpha_{ij}(\omega)} \cdot \mathcal{E}_j(\omega) + \frac{1}{2!}\boxed{\beta_{ijk}(\omega = \omega_1 + \omega_2)} \cdot \mathcal{E}_j(\omega_1) \cdot \mathcal{E}_k(\omega_2) + \frac{1}{3!}\boxed{\gamma_{ijkl}(\omega = \omega_1 + \omega_2 + \omega_3)} \cdot \mathcal{E}_j(\omega_1) \cdot \mathcal{E}_k(\omega_2) \cdot \mathcal{E}_l(\omega_3)$$

Examples:

- **Re [$\alpha(\omega)$]** - *linear refraction*
- **Im [$\alpha(\omega)$]** - *linear absorption*
- **Re [$\beta(\omega,\omega)$]** - *second harmonic generation*
- **Re [$\gamma(\omega,\omega,\omega)$]** - *third harmonic generation*
- **Im [$\gamma(\omega,0,0)$]** - *electro-absorption (Stark effect)*
- **Im [$\gamma(\omega,\omega,-\omega)$]** - *two-photon absorption*
- **Re [$\gamma(\omega,\omega,0)$]** - *EFISHG*
- *etc.*

How to calculate optical responses

Derivative (coupled-perturbed, CP) approaches:



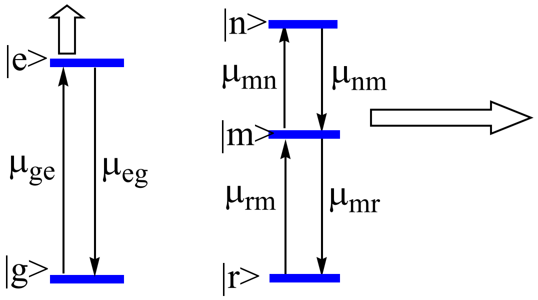
$$\alpha_{ij} = -\frac{\partial^2 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j} \qquad \beta_{ijk} = -\frac{\partial^3 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_k}$$

$$\gamma_{ijkl} = -\frac{\partial^4 E}{\partial \mathcal{E}_i \partial \mathcal{E}_j \partial \mathcal{E}_k \partial \mathcal{E}_l}$$

H. Sekino, R.J. Bartlett, J. Chem. Phys., 98, 3022 (1993)

Time-dependent (sum-over-state, SOS) approaches:

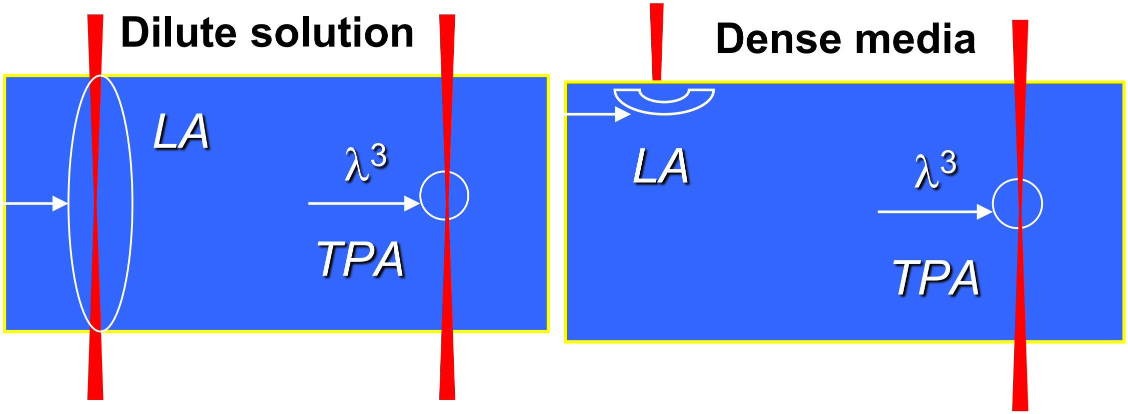
$$\alpha(\omega) = \sum_{e} \frac{2E_{ge}\mu_{ge}^2}{E_{ge}^2 - (\omega + \mathrm{i}\Gamma_{ge})^2}$$



$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{1}{6}\left(\frac{h}{2\pi}\right)^{-3} \sum_{\text{perm}} \left[\sum_{m,n,p(\neq r)} \frac{\langle r|\mu_i|m\rangle\langle m|\overline{\mu}_j|n\rangle\langle n|\overline{\mu}_k|p\rangle\langle p|\mu_l|r\rangle}{(\omega_{mr}-\omega_\sigma-i\Gamma_{mr})(\omega_{nr}-\omega_2-\omega_3-i\Gamma_{nr})(\omega_{pr}-\omega_3-i\Gamma_{pr})} - \sum_{m,n(\neq r)} \frac{\langle r|\mu_i|m\rangle\langle m|\mu_j|r\rangle\langle r|\mu_k|n\rangle\langle n|\mu_l|r\rangle}{(\omega_{mr}-\omega_\sigma-i\Gamma_{mr})(\omega_{nr}-\omega_3-i\Gamma_{nr})(\omega_{nr}+\omega_2-i\Gamma_{nr})} \right]$$

B.J. Orr, J.F. Ward, Mol. Phys. 20, 513 (1971) J.L. Bredas, et al. Chem. Rev., 94, 243 (1994)

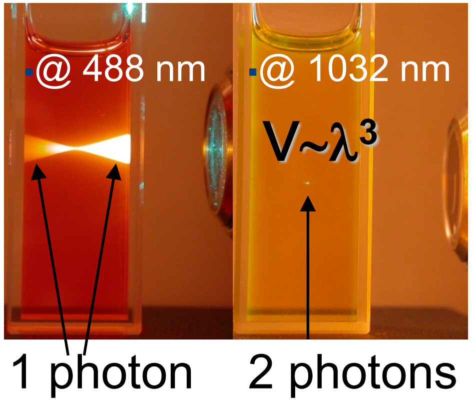
Case study 1: Non-linear spectroscopy, two-photon absorption

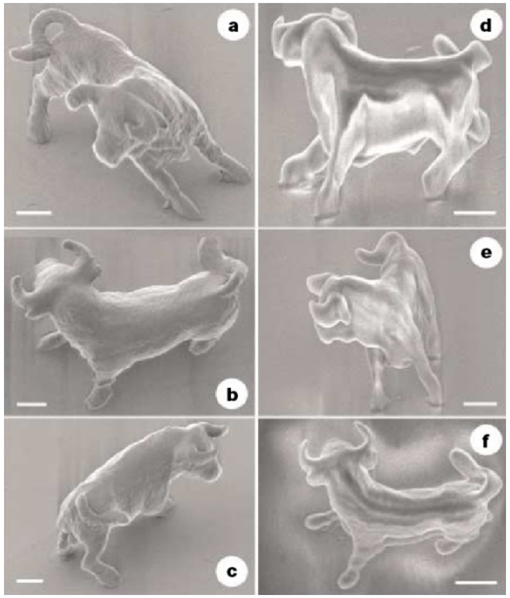


Linear vs. two photon absorption

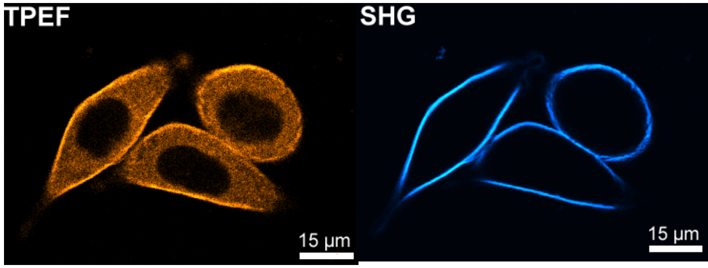
Linear Absorption (LA) $\sigma_{LA} \sim \mathrm{Im}\langle\alpha(\omega)\rangle \sim I$

Two-Photon Absorption (TPA) $\sigma_{TPA} \sim \mathrm{Im}\langle\gamma(\omega,\omega,-\omega)\rangle \sim I^2$



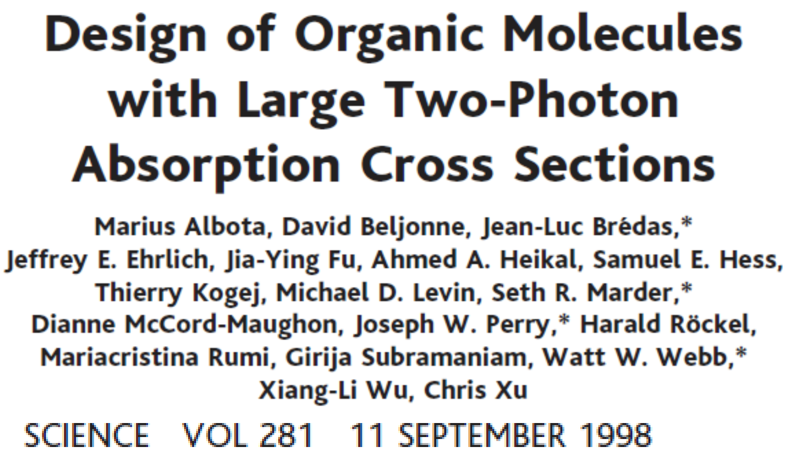


Microfabrication by TPA induced polymerization at subdiffraction-limit resolution: 7x10 μm (size of a blood cell) Kawata S, Sun HB, Tanaka T, Takada K: Nature, 412, 697 (2001)



Scanning fluorescence microscopy, in vivo imaging: J. Neuroscience, 24, 999 (2004)

Case study 1: Non-linear spectroscopy, two-photon absorption



Design of Organic Molecules with Large Two-Photon Absorption Cross Sections

Marius Albota, David Beljonne, Jean-Luc Brédas,*
Jeffrey E. Ehrlich, Jia-Ying Fu, Ahmed A. Heikal, Samuel E. Hess,
Thierry Kogej, Michael D. Levin, Seth R. Marder,*
Dianne McCord-Maughon, Joseph W. Perry,* Harald Röckel,
Mariacristina Rumi, Girija Subramaniam, Watt W. Webb,*
Xiang-Li Wu, Chris Xu

SCIENCE VOL 281 11 SEPTEMBER 1998

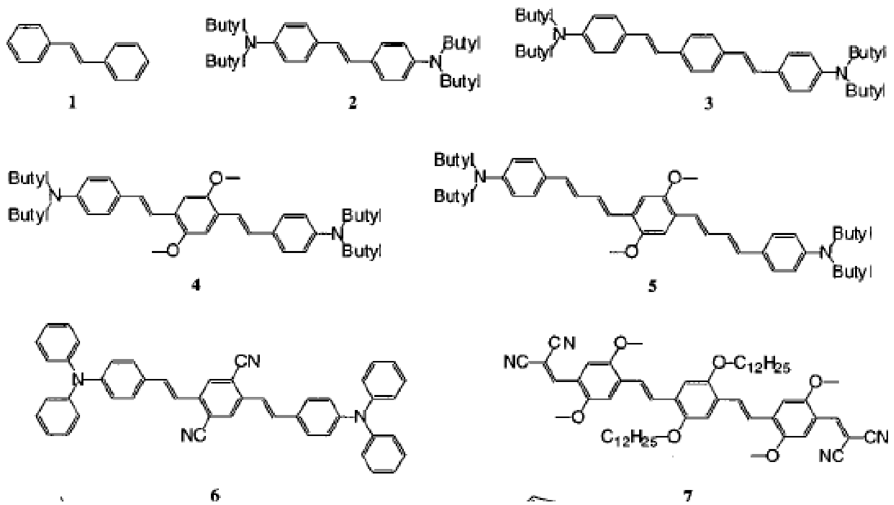


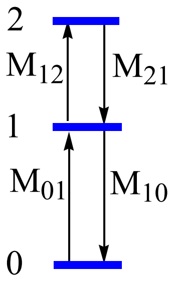
Figure 1: Molecular D-A-D and A-D-A structures

Ward and Orr sum-over-states expansion

$$\gamma_{ijkl}(-\omega_\sigma;\omega_1,\omega_2,\omega_3) = \frac{1}{6}\left(\frac{h}{2\pi}\right)^{-3}\sum_{\text{perm}}\left[\sum_{m,n,p(\neq r)} \frac{\langle r|\mu_i|m\rangle\langle m|\overline{\mu_j}|n\rangle\langle n|\overline{\mu_k}|p\rangle\langle p|\mu_l|r\rangle}{(\omega_{mr}-\omega_\sigma-i\Gamma_{mr})(\omega_{nr}-\omega_2-\omega_3-i\Gamma_{nr})(\omega_{pr}-\omega_3-i\Gamma_{pr})} - \sum_{m,n(\neq r)}\frac{\langle r|\mu_i|m\rangle\langle m|\mu_j|r\rangle\langle r|\mu_k|n\rangle\langle n|\mu_l|r\rangle}{(\omega_{mr}-\omega_\sigma-i\Gamma_{mr})(\omega_{nr}-\omega_3-i\Gamma_{nr})(\omega_{nr}+\omega_2-i\Gamma_{nr})}\right]$$

Approximate formulae

$$\delta_{S_0\rightarrow S_2} \propto \frac{M_{01}^2\,M_{12}^2}{(E_1-E_0-\hbar\omega)^2\Gamma}$$



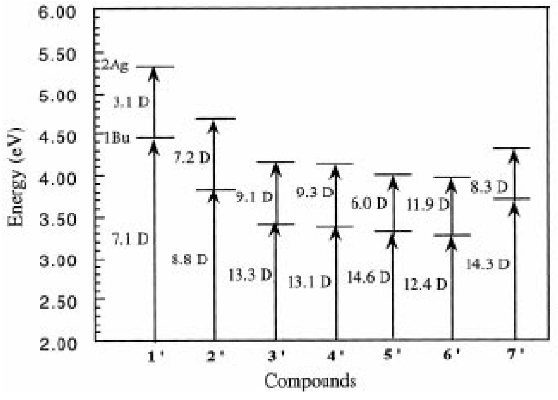
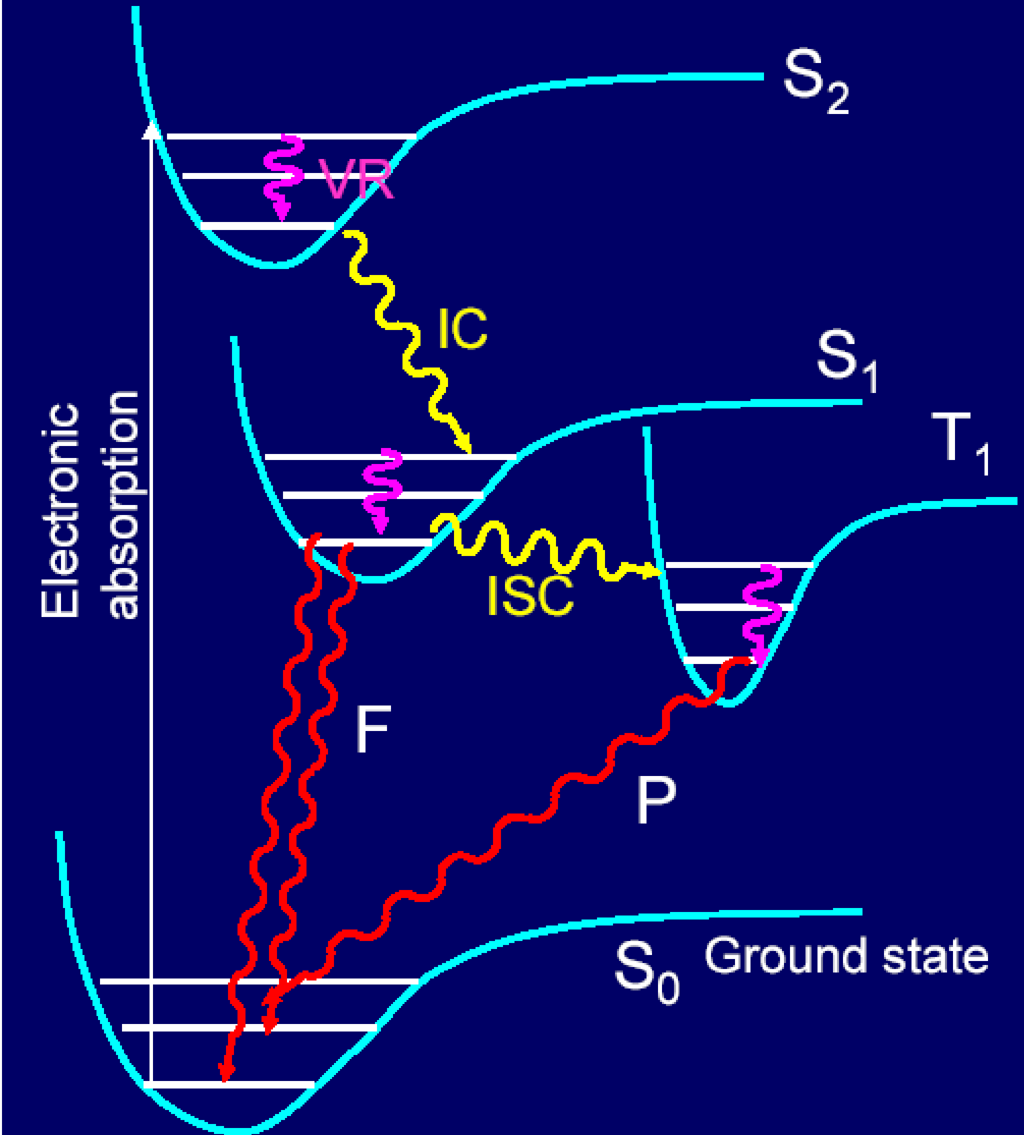


Fig. 2. Scheme of the calculated energy levels

Methods used: Semiempirical Models (ZINDO)

Properties of Absorption and Emission



Absorption starts from the lowest vibrational level of the ground state

Fluorescence is red shifted (called Stokes shift) and is independent of excitation wavelength

The lifetime of phosphorescence is much longer than that of fluorescence

Illustration 2: The Harmonic Oscillator

A particle subject to a restoring force (e.g. Hooke's Law)

$F = -kx$ ***i.e., a potential*** $V(x) = (1/2)kx^2$ ***Applies to a single particle or 2 particles with reduced mass μ***

The Schrodinger equation $-\frac{\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi(x) = E\psi(x)$

Solution

$$\psi_n(x) = N_n H_n(\alpha^{1/2}x)e^{-\alpha x^2/2} \qquad n = 0, 1, 2, \ldots$$

$$\alpha = \sqrt{\frac{k\mu}{\hbar^2}} \qquad N_n = \frac{1}{\sqrt{2^n n!}}\left(\frac{\alpha}{\pi}\right)^{1/4}$$

$$H_n(x) = (-1)^n e^{x^2}\frac{d^n}{dx^n}\left(e^{-x^2}\right)$$

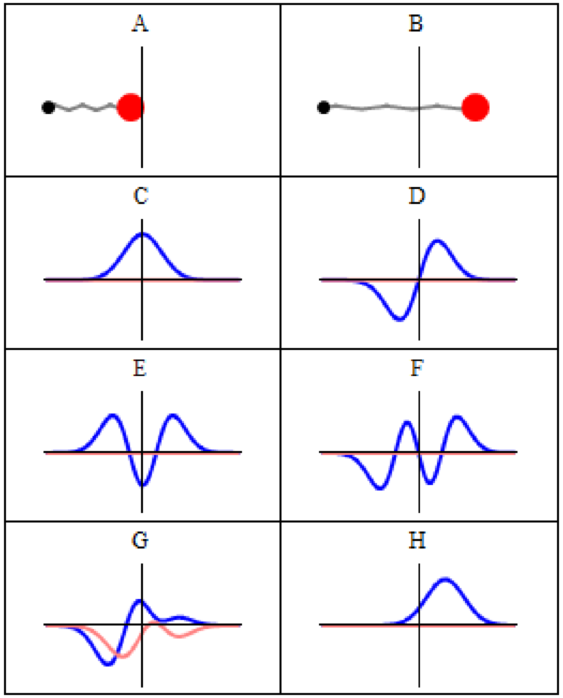
The Hermite polynomial of degree *n*

Energy levels:

$$E_n = \hbar\omega(n + 1/2)$$

$$\omega = \sqrt{k/\mu}$$

This model is foundational for ALL vibronic spectroscopy!!!!



Wikipedia: Some trajectories of a harmonic oscillator (i.e. a ball attached to a spring) in classical mechanics (A-B) and quantum mechanics (C-H). In quantum mechanics, the position of the ball is represented by a wave (wavefunction), with the real part shown in blue and the imaginary part shown in red. Some of the trajectories (such as C,D,E,and F) are standing waves (or "stationary states"). Each standing-wave frequency is proportional to a possible energy level of the oscillator. (G-H) are non-stationary states (G) is a randomly-generated superposition of the four states (C-F). H is a "coherent state" which somewhat resembles the classical state B.

Our toolbox

- Our material is composed from nuclei and electrons bound by Coulomb interactions
- Separate electronic (fast) from nuclei (slow) motion (adiabatic or Born-Oppenheimer approximation)
- Apply molecular mechanics FF (no electrons!) or
- Solve the Schrodinger equation for molecular electronic Hamiltonian:

$$\left[-\frac{1}{2}\sum_i \nabla_i^2 - \sum_{iA}\frac{Z_A}{r_{iA}} + \sum_{i>j}\frac{1}{r_{ij}}\right]\psi_e(\mathbf{r};\mathbf{R}) = E_e\psi_e(\mathbf{r};\mathbf{R})$$

Method	*Hamiltonian*	*Wavefunction*	*Cost*
Ab initio *(e.g. HF, CAS-CI, CC-EOM)*	*Exact*	*Approximate* *(All electronic correlations)*	*Large* *(~10 atoms)*
Density Functional *(e.g. DFT, TDDFT)*	*Approximate,* $F(\rho)$*,* *(All electronic correlations)*	*Fixed* *(Kohn-Sham system, mean field)*	*Significant* *(~100 atoms)*
Semiempirical *(e.g. AM1, MNDO, INDO/S)*	*Approximate,* *(Some electronic correlations)*	*Approximate* *(Some electronic correlations)*	*Low* *(~1000 atoms)*
Tight-binding *(e.g. Huckel, Frenkel, SSH)*	*Approximate,* *(Min electronic correlations)*	*Approximate* *(Usually uncorrelated)*	*Low* *(~10,000 atoms)*
Molecular Mechanics *(e.g. MM2, AMBER)*	*None,* *(just PES mapping R->E)*	*None* *(electrons are not there)*	*Very Low* *(~100,000 atoms)*

Nuclei (or vibrational) degrees of freedom

Taylor expansion of energy (i.e. PES) near equilibrium:

$$E(R) = E(R_0) + \frac{\mathrm{d}E}{\mathrm{d}R}(R - R_0) + \frac{1}{2}\frac{\mathrm{d}^2E}{\mathrm{d}R^2}(R - R_0)^2 + \frac{1}{6}\frac{\mathrm{d}^3E}{\mathrm{d}R^3}(R - R_0)^3 + \cdots$$

Can be taken as 0

Vanishes

Quadratic

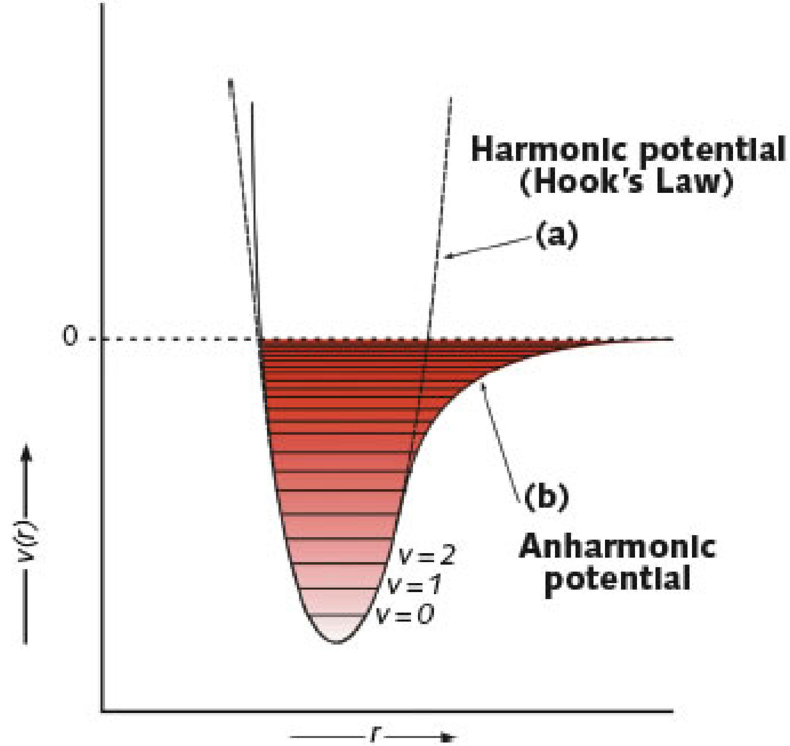
Cubic anharmonicity

$$E(\Delta R) \cong \frac{1}{2}\frac{\mathrm{d}^2E}{\mathrm{d}R^2}\Delta R^2 = \tfrac{1}{2}k\Delta R^2$$

Generally, molecular system with M-nuclei has 3N-6 internal degrees of freedom.

3 rotational and 3 translational degrees of freedom

3N-6 internal degrees of freedom are naturally represented as vibrational normal modes.



Vibrational normal coordinates

Change of coordinate system (unitary transformation)

$$\mathbf{x}' = \mathbf{U}\mathbf{x}$$

$$\mathbf{x} = \mathbf{U}^{-1}\mathbf{x}'$$

$\mathbf{U}^{-1}\mathbf{U}$ Unit matrix

2 variables

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

Hessian matrix

$$\begin{pmatrix} \frac{\partial^2 E}{\partial x_1^2} & \frac{\partial^2 E}{\partial x_1 \partial x_2} & \cdots \\ \frac{\partial^2 E}{\partial x_2 \partial x_1} & \frac{\partial^2 E}{\partial x_2^2} & \cdots \\ \vdots & \vdots & \ddots \end{pmatrix}$$

Need to change the coordinate system the make Hessian to be diagonal and Schrodinger equation for nuclei to be simple:

$$V(\mathbf{x}) \approx \tfrac{1}{2}(\mathbf{x}-\mathbf{x}_0)^{\mathrm{t}} \left(\frac{d^2 V}{d\mathbf{x}^2} \right) (\mathbf{x}-\mathbf{x}_0) = \tfrac{1}{2} \Delta\mathbf{x}^{\mathrm{t}} \mathbf{F} \Delta\mathbf{x}$$

$$\left[-\sum_{i=1}^{3N_{\mathrm{atom}}} \left(\frac{1}{2m_i} \frac{\partial^2}{\partial x_i^2} \right) + \tfrac{1}{2} \Delta\mathbf{x}^{\mathrm{t}} \mathbf{F} \Delta\mathbf{x} \right] \Psi_{\mathrm{nuc}} = E_{\mathrm{nuc}} \Psi_{\mathrm{nuc}}$$

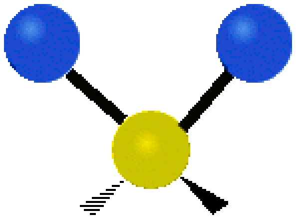
Step 1: mass-dependent coordinates $y_i = \sqrt{m_i}\,\Delta x_i$ $\quad \frac{\partial^2}{\partial y_i^2} = \frac{1}{m_i} \frac{\partial^2}{\partial x_i^2}$ $\quad G_{ij} = \frac{1}{\sqrt{m_i m_j}}$

Step 2: normal modes coordinates $q = Uy$ Here *U* diagonilizes $\mathbf{F} \cdot \mathbf{G}$

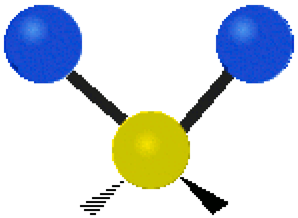
Finally: $\left[-\sum_{i=1}^{3N_{\mathrm{atom}}} \left(\frac{1}{2} \frac{\partial^2}{\partial q_i^2} + \frac{1}{2} \varepsilon_i q_i^2 \right) \right] \Psi_{\mathrm{nuc}} = E_{\mathrm{nuc}} \Psi_{\mathrm{nuc}}$ $\quad \nu_i = \frac{1}{2\pi} \sqrt{\varepsilon_i}$ Vibrational frequencies

Gallery of molecular vibrations

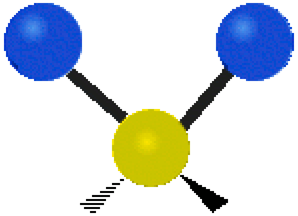
Symmetrical stretching



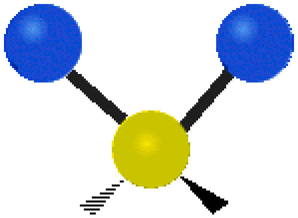
Antisymmetrical stretching



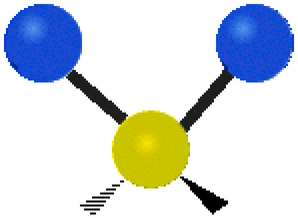
Scissoring



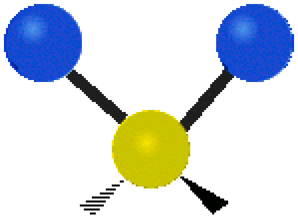
Rocking



Wagging

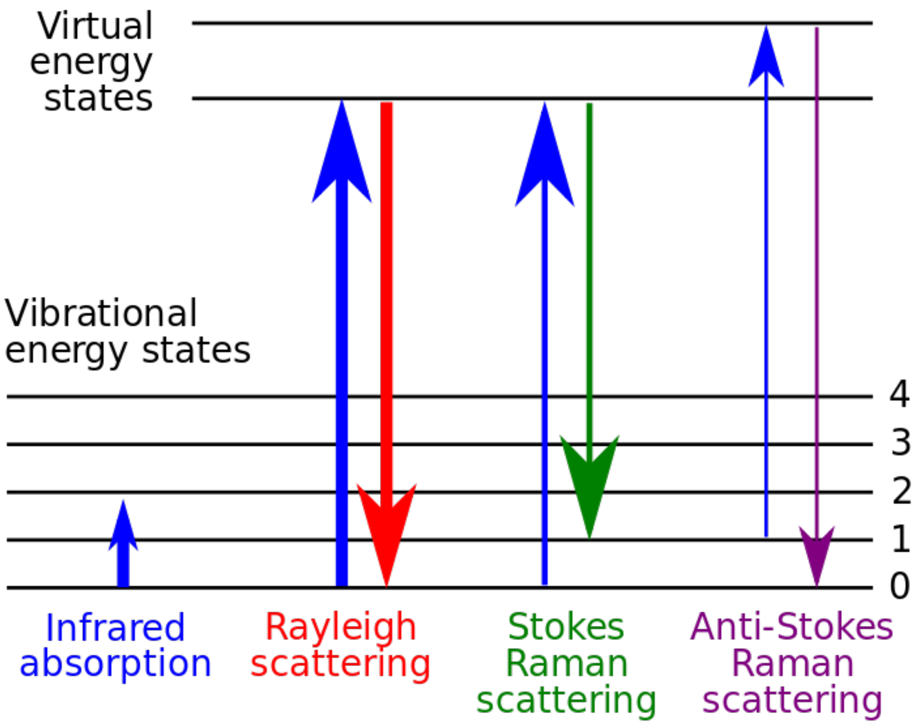


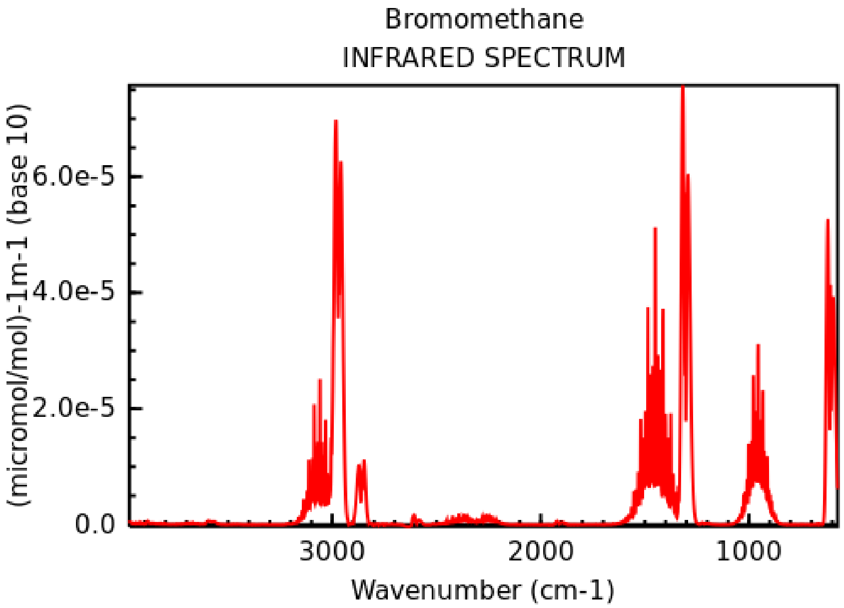
Twisting



From Wikipedia: typical types of vibrational motion in smaller molecules

Vibrational spectroscopy



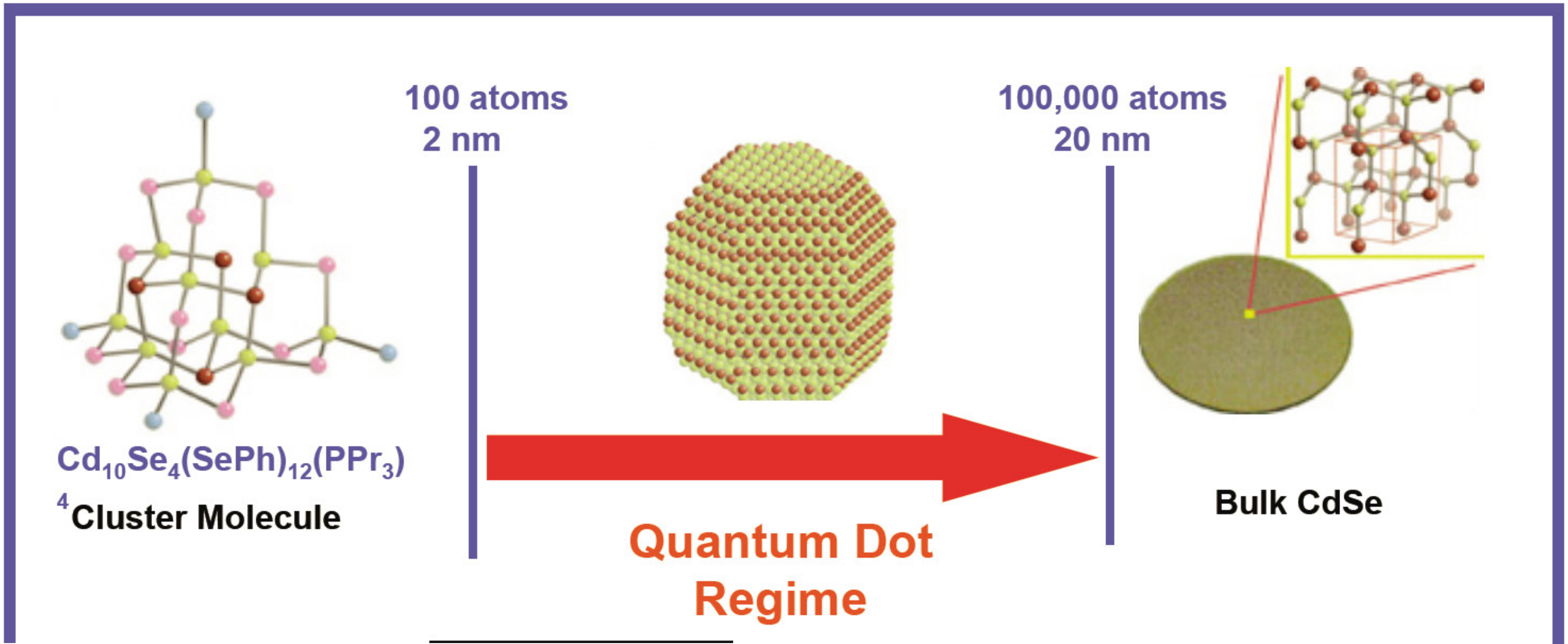

Bromomethane
INFRARED SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

$$\text{IR intensity} \propto \left(\frac{\partial \mu}{\partial \mathbf{q}}\right)^2 \propto \left(\frac{\partial^2 E}{\partial \mathbf{R} \partial \mathbf{F}}\right)^2$$

$$\text{Raman intensity} \propto \left(\frac{\partial \alpha}{\partial \mathbf{q}}\right)^2 \propto \left(\frac{\partial^3 E}{\partial \mathbf{R} \partial \mathbf{F}^2}\right)^2$$

Practice 1: Semiconductor Nanocrystals or Quantum Dots



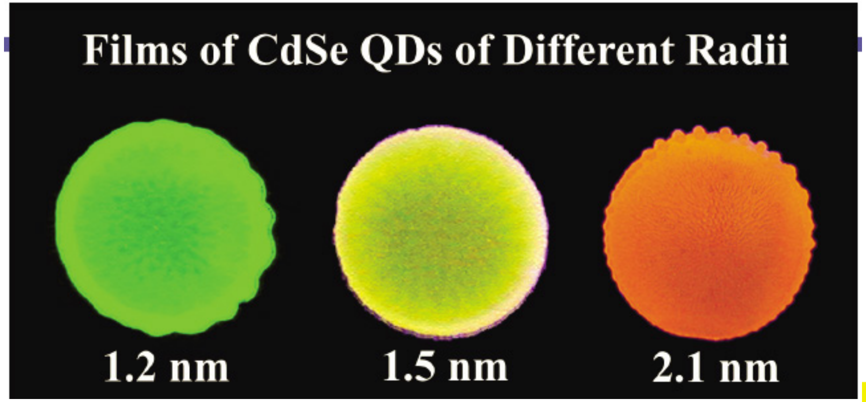
100 atoms
2 nm

100,000 atoms
20 nm

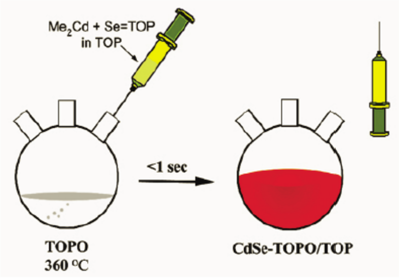
$Cd_{10}Se_4(SePh)_{12}(PPr_3)_4$
Cluster Molecule

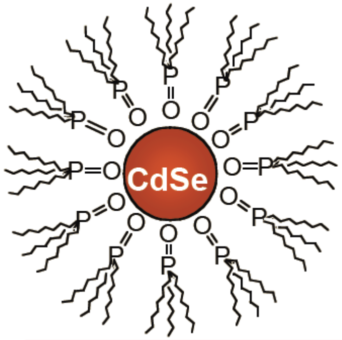
Quantum Dot Regime

Bulk CdSe



- **CdSe NQDs**



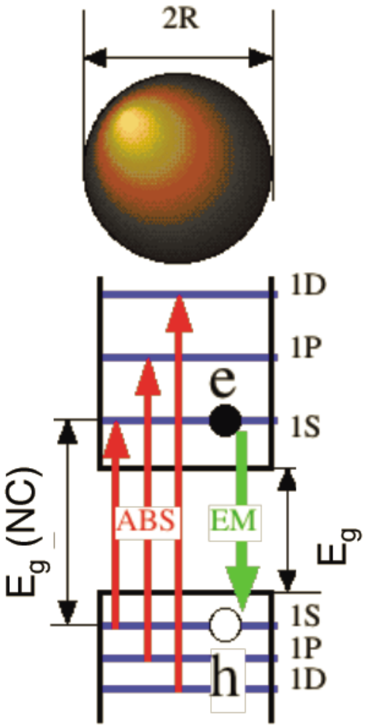


R = 10—50 Å, δR/R = 4—7%

C. Murray, D. Norris, and M. Bawendi, *J. Am. Chem. Soc.* **115**, 8706 (1993).

Practice 1: Energy Structures in Nano-crystals: almost an atom but not quite

- **Spherical quantum-well model**



•Discrete Energy States:

$$E_{nl} = \frac{\hbar^2 \beta_{nl}^2}{2mR^2}$$

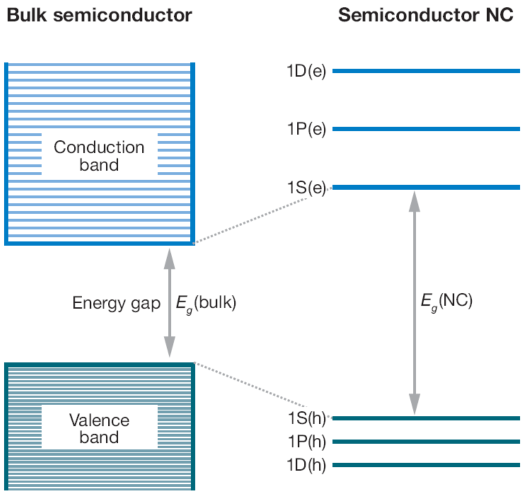
$n = 1,2,3\ldots, l = 0(s), 1(p), 2(d)\ldots$

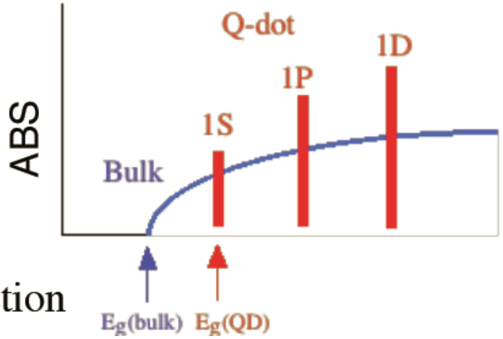
•Energy Gap:

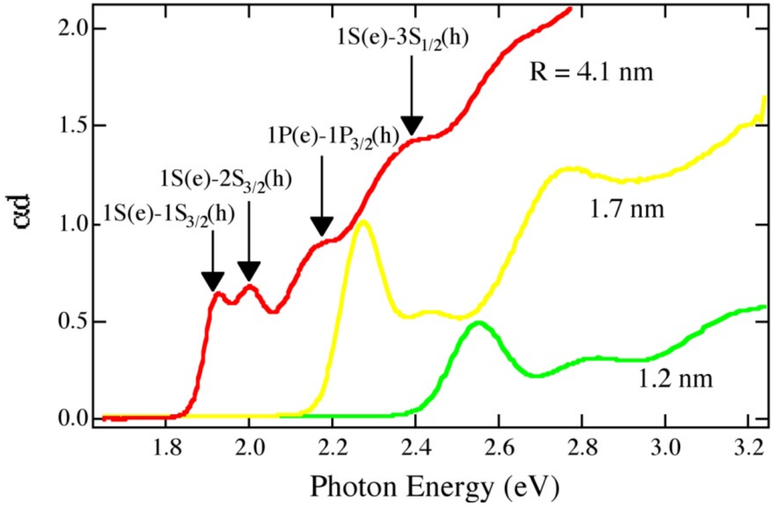
$$E_g(QD) = E_g(bulk) + \frac{\hbar^2 \pi^2}{2m_{eh}R^2}$$

$CdSe \quad QDs: \quad E_g = 1.7eV \Rightarrow 3.2\,eV$

$R = 20\,nm \Rightarrow 1.5\,nm$







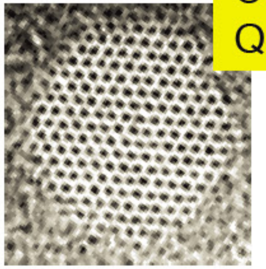
$\Psi = \phi_B \Phi_{nlm}$

ϕ_B – Bloch function

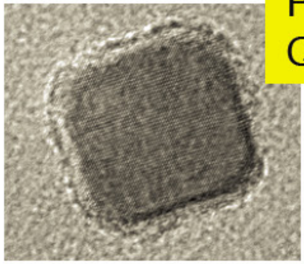
Φ_{nlm} – envelope function

Practice 1: Chemically engineered building blocks

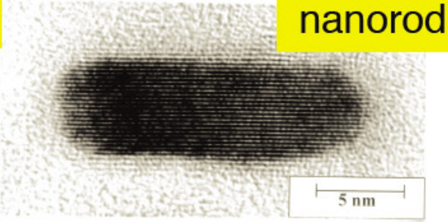
- **Tunable sizes/shapes**



CdSe Q-dots



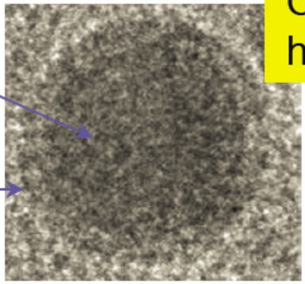
PbSe Q-cubes



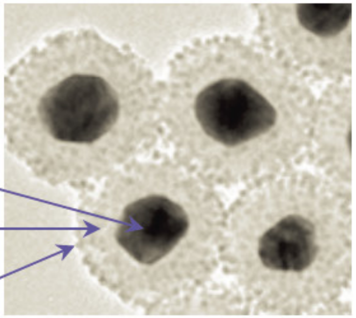
Co nanorods

- **Complex hetero-structures**

H. Kim *et al.*, *J. Am. Chem. Soc.* **127**, 544 (2005)



Co/CdSe hetero-NCs

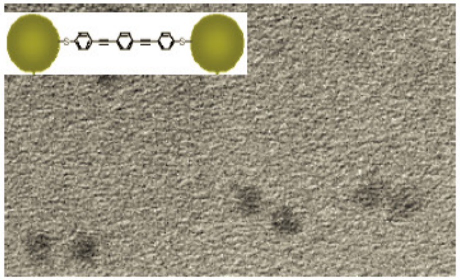


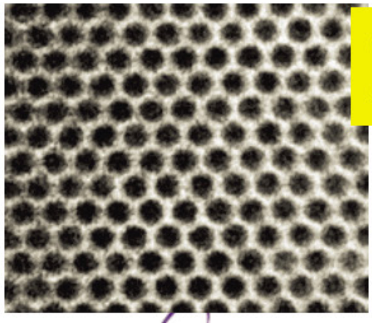
Au/Silica/CdSe NQD superstructures

N. Liu et al. *J. Am. Chem. Soc.* **128**, 15362 (2006)

- **Controlled assembly**

Q-dot molecules

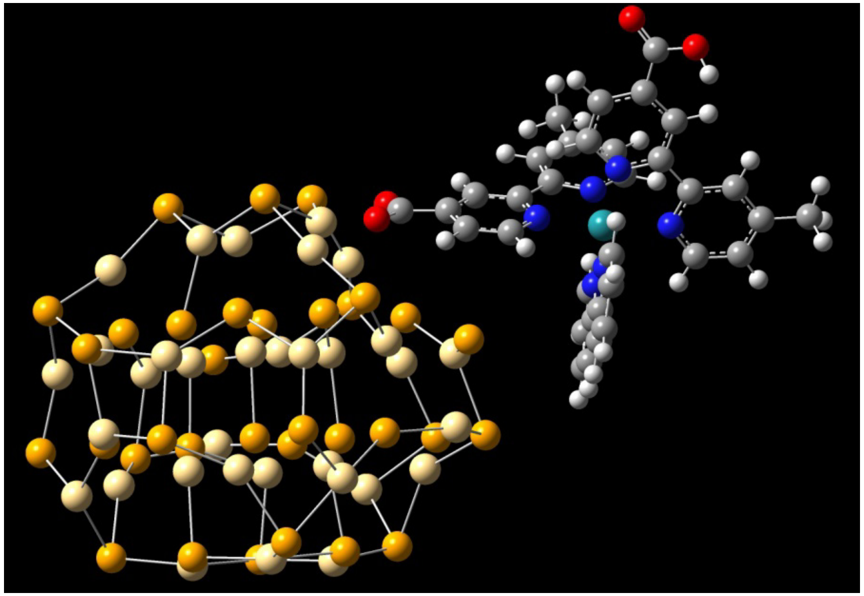


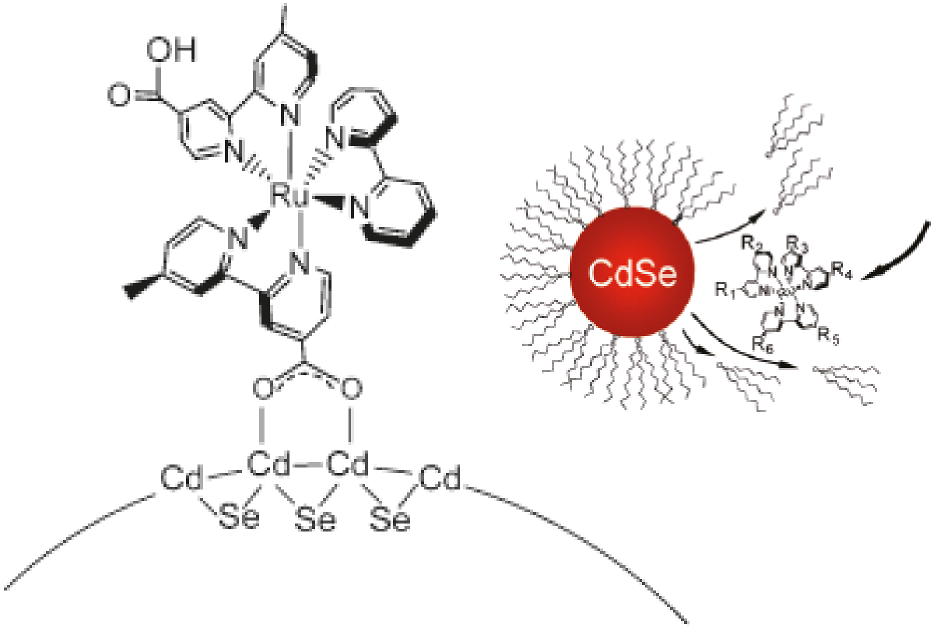


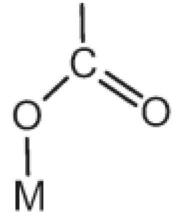
Q-dot solids

Practice 1: Functionalizing surface in QDs

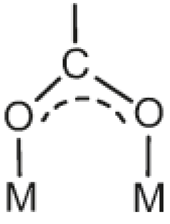
Experimentalist: I am trying to functionalize the surface of CdSe QDs with Ru-dyes. Can you help me to understand how the dyes will bind to the surface?



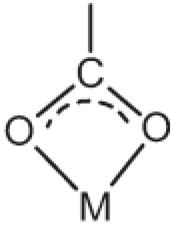




Unidentate



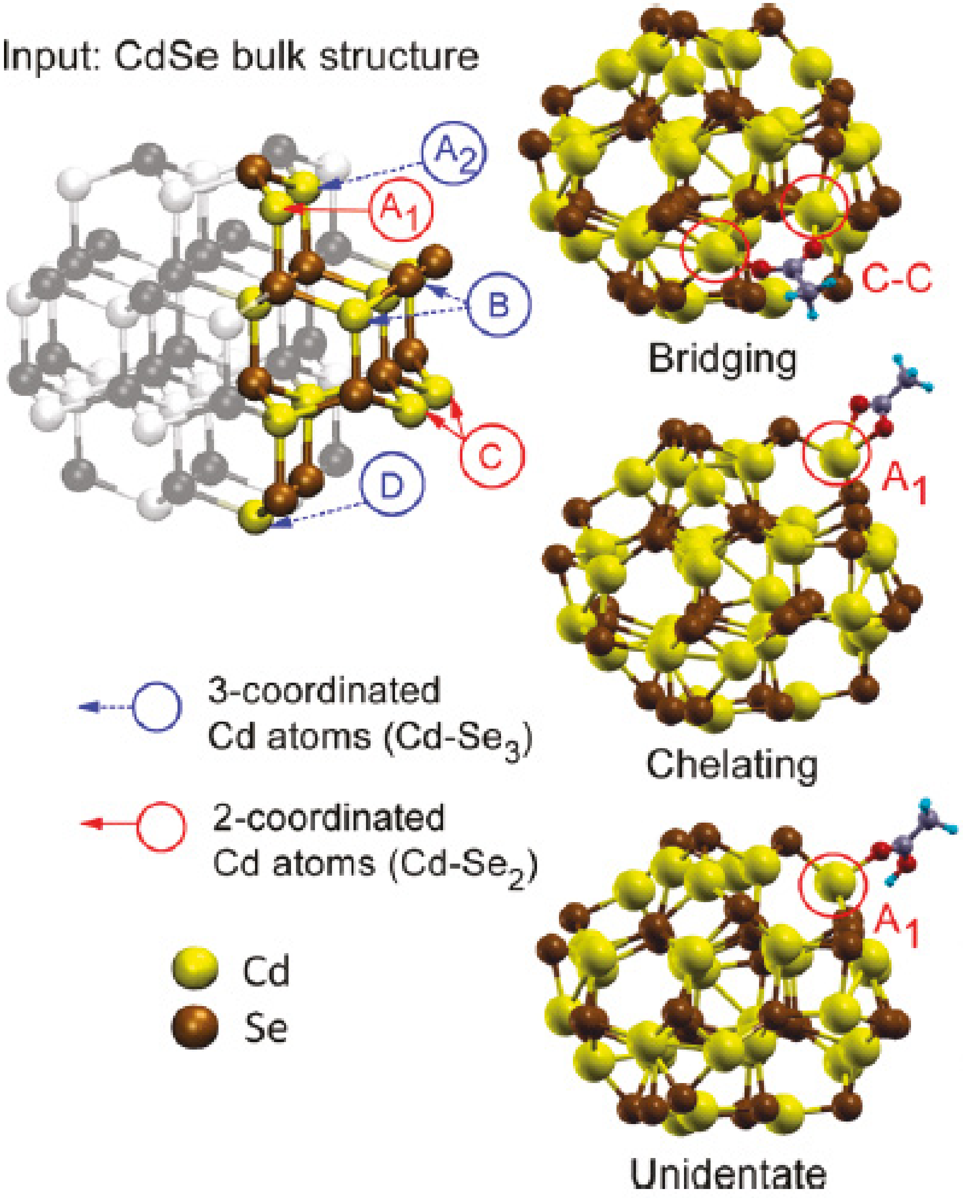
Bridging



Chelating

Practice 1: Theory – how to approach…

Cut a small cluster from the bulk (here Cd33Se33) and attach a single ligand to the surface at different position (relying on the chemical intuition of our friend-experimentalist)



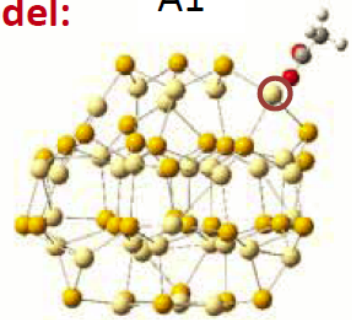
Practice 1: Theory – bridging is preferable!

$E_{binding} = E(QD+COO^-)^{opt} - E(QD)^{opt} - E(COO^-)^{opt}$; Optimization is done by B3LYP/LANL2DZ

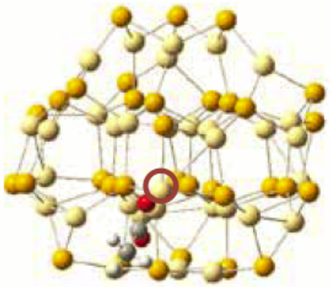
Bi-dentate model:

🟫 Selenium
🟨 Cadmium

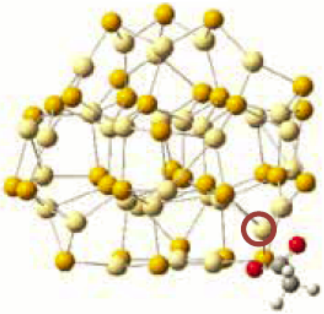
A1



C1



C2



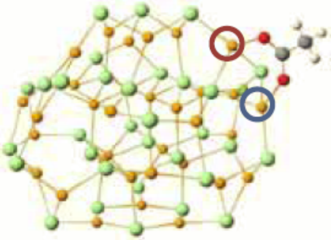
	A1	C1	C2
Cd-O (Ang):	2.30 & 2.37	2.35 & 2.33	2.40 & 2.30
Eb (eV): vac/solv	**-3.80/-0.45**	**-3.73/-0.45**	**-2.98/-0.17**
Eb (eV): solv-opt	**-0.56**		
Egap (eV):	2.66	2.14	2.01

Bridging model:

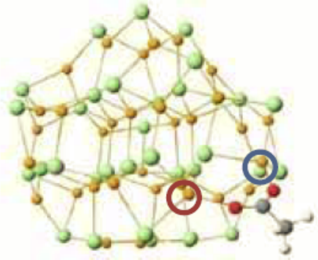
🟩 Selenium
🟧 Cadmium

A1-A1

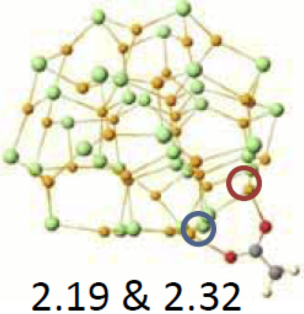
A1-B



C-B



C-D



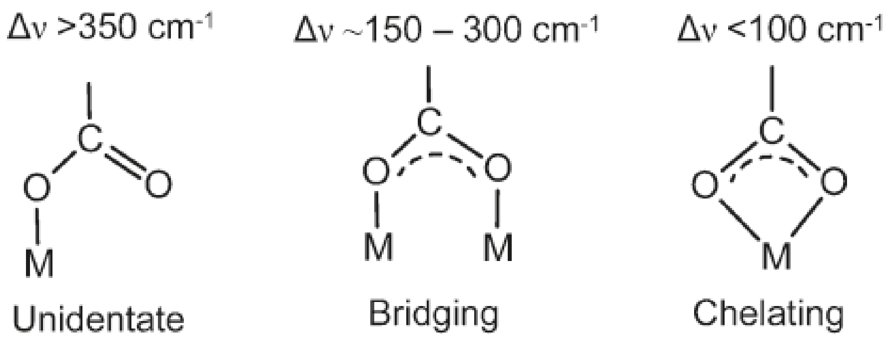
	A1-A1	A1-B	C-B	C-D
Cd-O (Ang):	2.45 & 2.19	2.21 & 2.25	2.19 & 2.20	2.19 & 2.32
Eb (eV): vac/solv	**-4.53/-0.70**	**-4.31/-0.55**	**-4.52/-0.51**	**-3.25**
Eb (eV): solv-opt	**-0.80**	**-0.74**	**-0.63**	
Egap (eV):	2.78	2.53	2.20	1.88

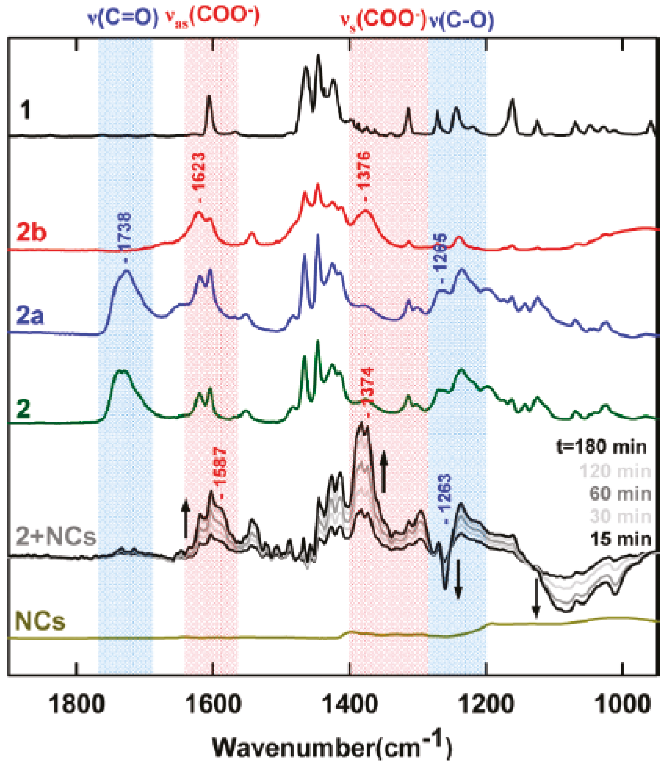
Practice 1: Experiment – vibrational spectroscopy confirm bridging binding

Formation of Assemblies Comprising Ru–Polypyridine Complexes and CdSe Nanocrystals Studied by ATR-FTIR Spectroscopy and DFT Modeling

Langmuir 2011, 27, 8377–8383

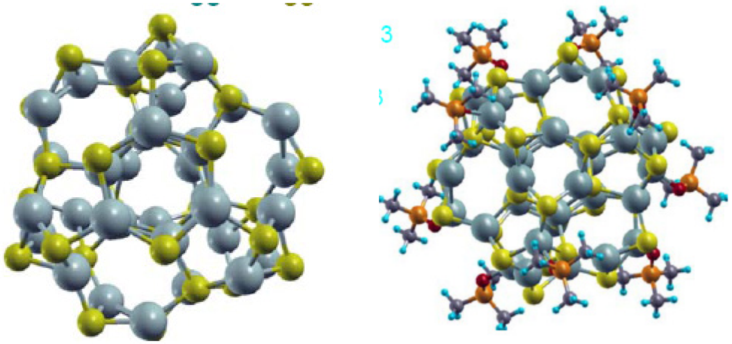
Alexey Y. Koposov,[†] Thomas Cardolaccia,[§] Victor Albert,[‡] Ekaterina Badaeva,[‡] Svetlana Kilina,[‡] Thomas J. Meyer,[§] Sergei Tretiak,[‡] and Milan Sykora*,[†]

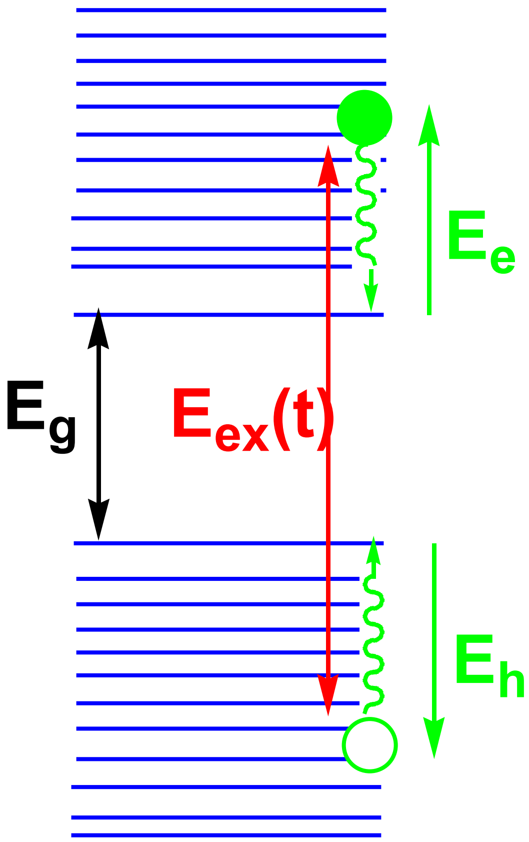


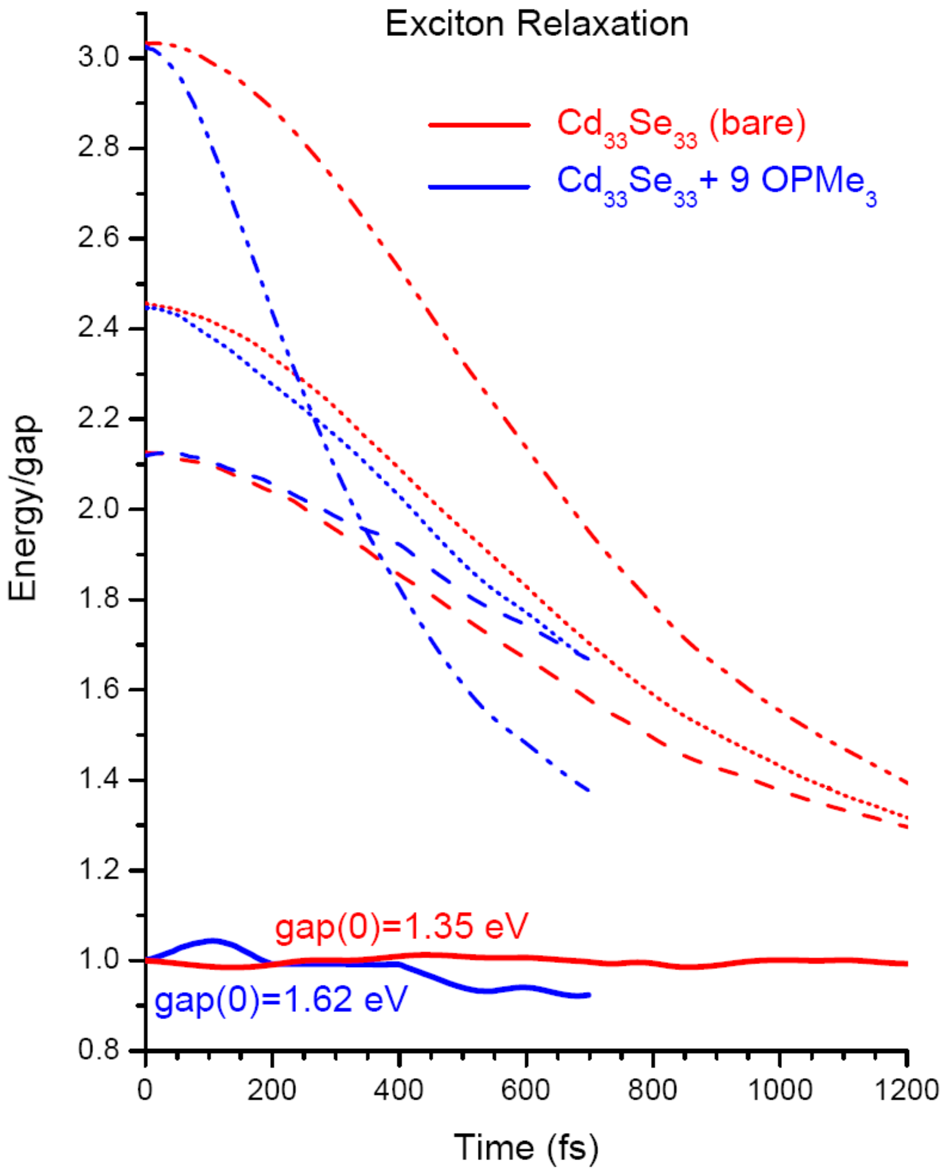


Possible Modes of Attachment of the Carboxylic Acids to Semiconductor Surfaces and Corresponding Difference in Frequencies of Symmetric and Asymmetric Stretches of the Carboxylic Acid Group

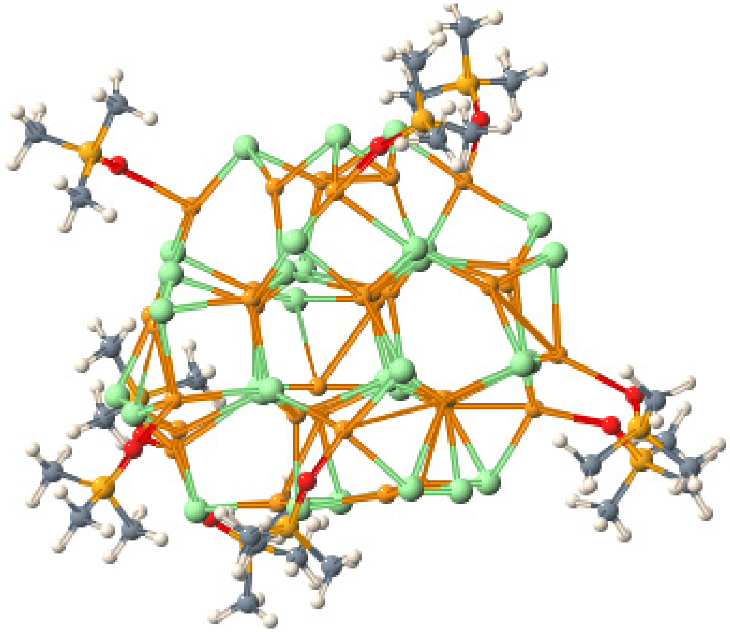
Case study 1: The role of ligands in NR relaxation







Case study 1: The role of ligands in NR relaxation



Gap

Photoexcitation energy

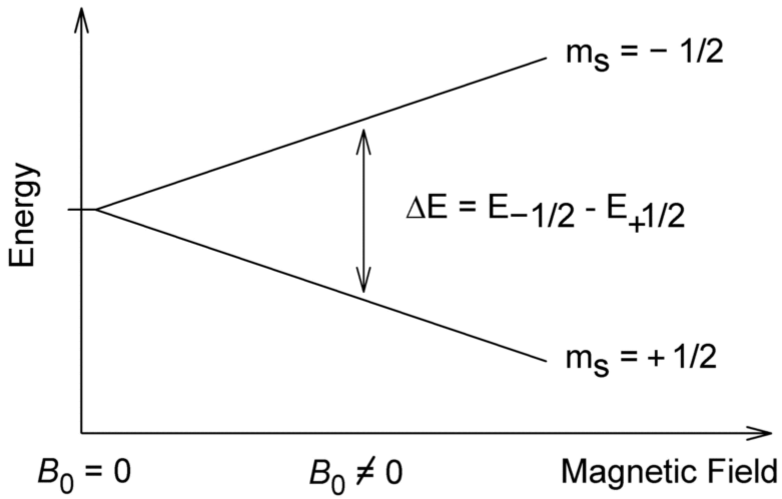
S. Kilina, S. Ivanov, and S. Tretiak, J. Am. Chem. Soc. 131, 7717 (2009)
S. Kilina, K. Velizhanin S. Ivanov. O.V. Prezhdo, S. Tretiak ACS Nano 5, 5233 (2011)

Nuclear magnetic resonance (NMR) spectroscopy

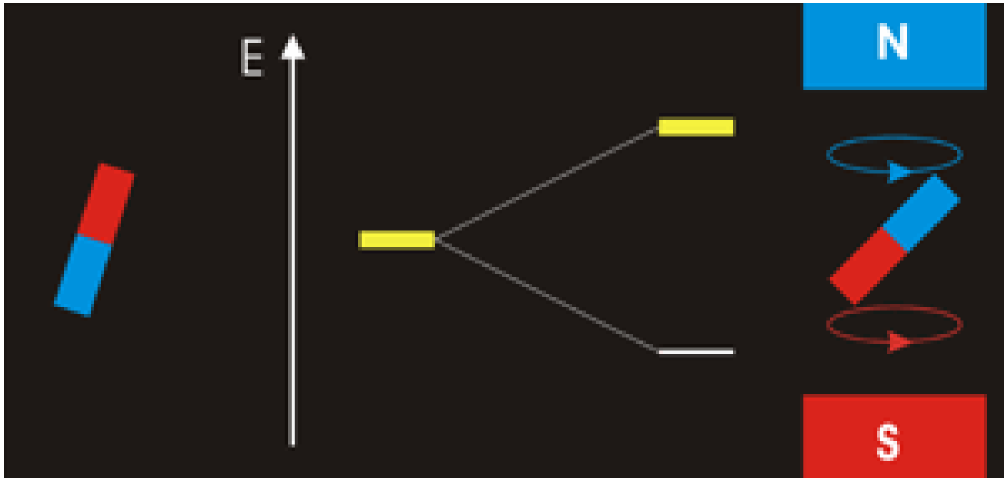
- NMR measurements assess the energy difference between a system in the presence and absence of an external magnetic field.

- The chemical shift is the resonant frequency of a nucleus relative to a standard.

- For a chemical shift measurement on a given nucleus, there are two magnetic fields of interest: the external field of the instrument and the internal field of the nucleus.

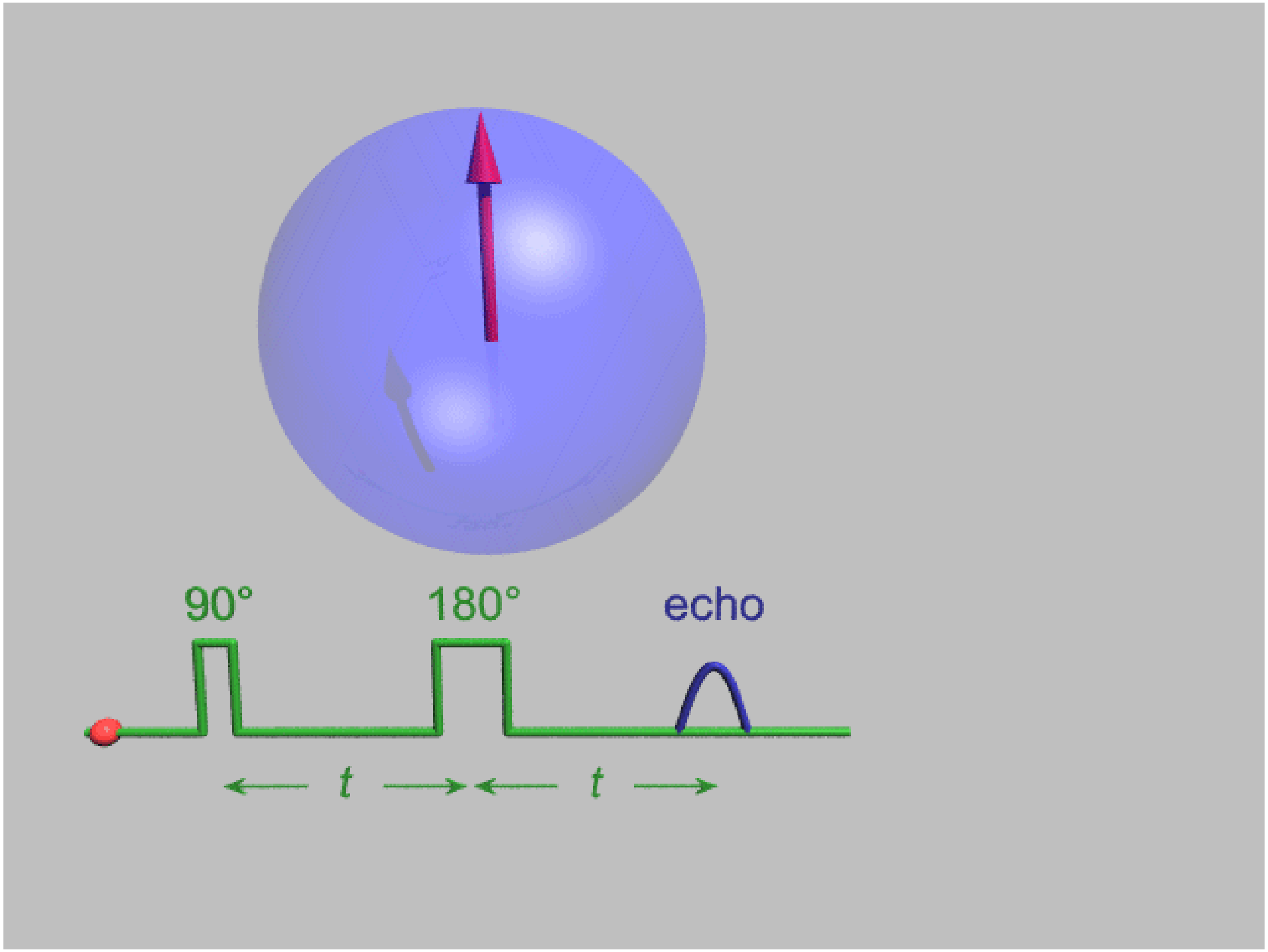


Wikipedia: Splitting of nuclei spin states in an external magnetic field



Wikipedia: the orientation of the magnetic moment can precess relative to the external field

Echo spectroscopies



Wikipedia: fantastic illustration of the spin echo and the photon echo

Chemical shift calculation

Chemical shift definition (parts per million, ppm):

$$\delta = \frac{\text{difference between a resonance frequency and that of a reference substance}}{\text{operating frequency of the spectrometer}}$$

For a chemical shift measurement on a given nucleus, there are two magnetic fields of interest: the external field of the instrument and the internal field of the nucleus. The chemical shift is proportional to the second derivative of the energy with respect to these two fields, and it can be computed using second-derivative technique.

The mixed derivative of an external and a nuclear magnetic field (nuclear spin) is the NMR shielding tensor σ. The corresponding quantity related to the electron spin is the ESR g-tensor

$$\text{NMR shielding} \propto \left(\frac{\partial^2 E}{\partial \mathbf{B} \partial \mathbf{I}}\right)$$

E-energy, B-external magnetic field,
I-internal magnetic moment

Table 9.5 Absolute chemical shifts (ppm) from various levels of theory.[a]

Molecule	Nucl	MB3[b]	HF	MP2	LDA	BLYP	BP86[c]	B3LYP	PBE1PBE[d]	B97-2[e]	Expt.
CH_4	^{13}C	189.4	195.7	201.5	193.7	187.5	191.2	189.6	194.0	190.7	195.1
	^{1}H	29.9					31.4				30.6
C_2H_2	^{13}C	100.4	113.9	123.3	100.0	105.7	110.4	106.3	114.0	113.9	117.2
	^{1}H	27.3					30.4				29.3

Derivative technique (Jensen):

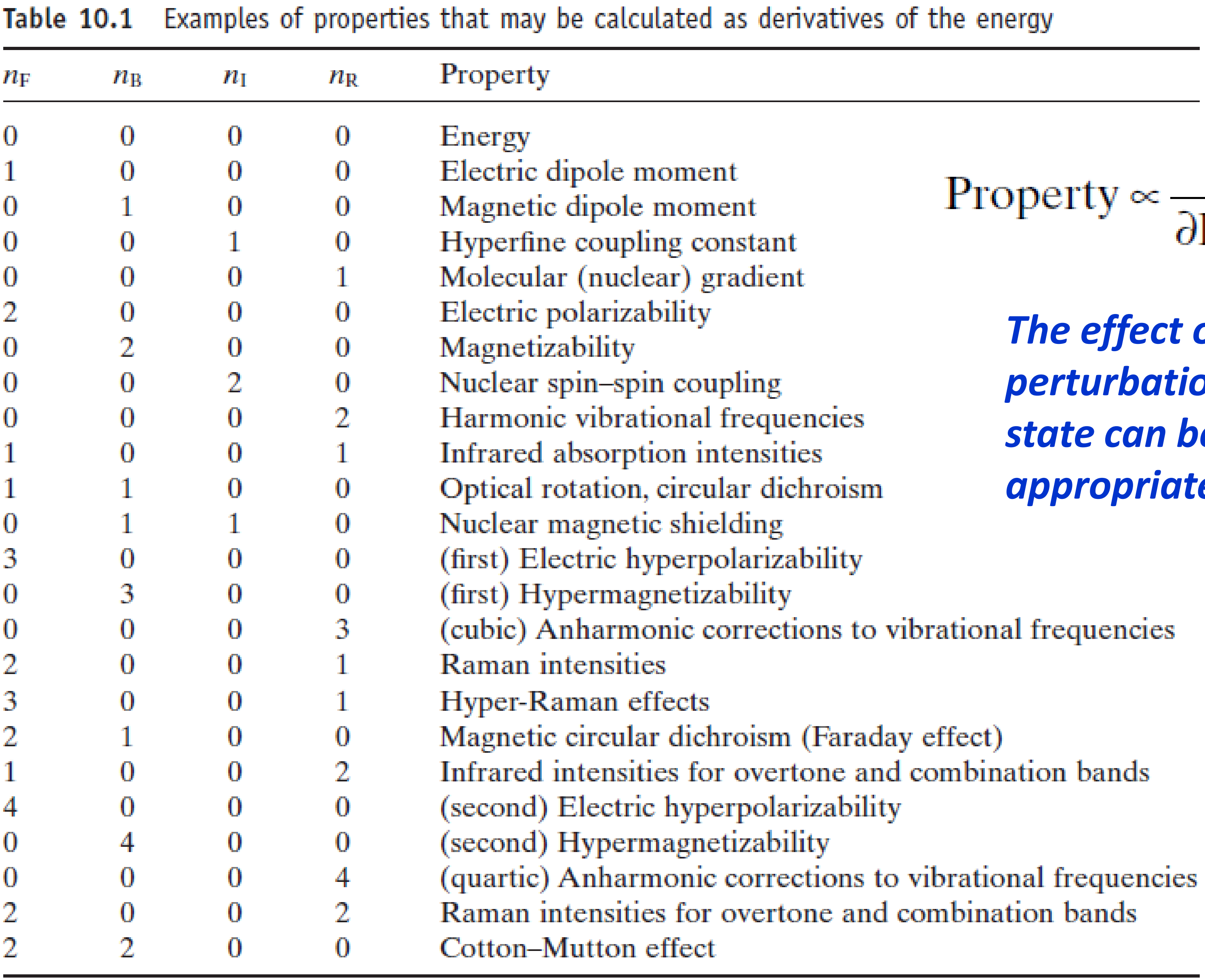


Table 10.1 Examples of properties that may be calculated as derivatives of the energy

n_F	n_B	n_I	n_R	Property
0	0	0	0	Energy
1	0	0	0	Electric dipole moment
0	1	0	0	Magnetic dipole moment
0	0	1	0	Hyperfine coupling constant
0	0	0	1	Molecular (nuclear) gradient
2	0	0	0	Electric polarizability
0	2	0	0	Magnetizability
0	0	2	0	Nuclear spin–spin coupling
0	0	0	2	Harmonic vibrational frequencies
1	0	0	1	Infrared absorption intensities
1	1	0	0	Optical rotation, circular dichroism
0	1	1	0	Nuclear magnetic shielding
3	0	0	0	(first) Electric hyperpolarizability
0	3	0	0	(first) Hypermagnetizability
0	0	0	3	(cubic) Anharmonic corrections to vibrational frequencies
2	0	0	1	Raman intensities
3	0	0	1	Hyper-Raman effects
2	1	0	0	Magnetic circular dichroism (Faraday effect)
1	0	0	2	Infrared intensities for overtone and combination bands
4	0	0	0	(second) Electric hyperpolarizability
0	4	0	0	(second) Hypermagnetizability
0	0	0	4	(quartic) Anharmonic corrections to vibrational frequencies
2	0	0	2	Raman intensities for overtone and combination bands
2	2	0	0	Cotton–Mutton effect

$$\text{Property} \propto \frac{\partial^{n_F+n_B+n_I+n_R} E}{\partial \mathbf{F}^{n_F}\, \partial \mathbf{B}^{n_B}\, \partial \mathbf{I}^{n_I}\, \partial \mathbf{R}^{n_R}}$$

The effect of small perturbations to the ground state can be calculated via appropriate derivatives

Discussion

1. **Why Intersystem crossing is molecular materials is relatively slow process compared to internal conversion? Is this the case for semiconductors with heavy elements? (CdSe or halide perovskites)**

2. **Why phosphorescence is a long-lived process? (can last for hours). Give an example.**

3. **What would be signatures of anharmonicities in vibrational spectra?**

4. ***Derivative technique applied to energy is very powerful way to get observables. What are the limitations?**

Individual studies:

- ***Reading.***

Required: *Cramer (14.1-14.5),*
Additional: *Jensen (10.1.1, 10.6, 10.9)*

Required: *Jensen (10.1, 16.2), Cramer (9.4)*
Additional: *Cramer (9.3)*