Quantum Chemistry Crash Course

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Contents

• ground-state methods: HF, DFT
• properties: geometries, frequencies (IR, Raman), charges
• simple excited-state methods, UV/vis-spectra

NOT contained:

introductions to:

• various software packages: Gaussian, Molpro, Turbomole, Orca, ADF, VASP,. . . : capabilities, generating input, understanding output, plotting/visualization of results, licenses,. . .
• available hardware: group-local clusters, institute clusters, computing center (RZ@CAU), HLRN: capabilities, getting access, reasonable usage, queueing systems, parallelization, how to write input, how to understand output, computer time proposals (HLRN),. . .
recommended literature


TDDFT: original/review papers

Molecular Hamiltonian

Time-independent molecular Schrödinger equation:

$$\hat{H}\Psi^{(k)}_{mol} = \mathcal{E}_k \Psi^{(k)}_{mol}$$

(1)

where $\hat{H}$ is the Hamilton operator for $N$ electrons and $K$ nuclei (in atomic units):

$$\hat{H} = -\sum_{A=1}^{K} \frac{1}{2M_A} \nabla^2_A \text{ kinetic energy of the nuclei } = \hat{T}_N$$

(2)

$$- \sum_{i=1}^{N} \frac{1}{2} \nabla^2_i \text{ kinetic energy of the electrons}$$

(3)

$$+ \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} \text{ Coulomb repulsion between electrons}$$

(4)

$$- \sum_{i=1}^{N} \sum_{A=1}^{K} \frac{Z_A}{r_{iA}} \text{ Coulomb attraction nuclei–electrons}$$

(5)

$$+ \sum_{A=1}^{K} \sum_{B>A}^{K} \frac{Z_A Z_B}{R_{AB}} \text{ Coulomb repulsion between nuclei}$$

(6)
Molecular Hamiltonian: conclusions for using it

\[
\hat{H} = -\sum_{A=1}^{K} \frac{1}{2M_A} \nabla^2_A - \sum_{i=1}^{N} \frac{1}{2} \nabla^2_i + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{1}{r_{ij}} - \sum_{i=1}^{N} \sum_{A=1}^{K} \frac{Z_A}{r_{iA}} + \sum_{A=1}^{K} \sum_{B>A}^{K} \frac{Z_A Z_B}{R_{AB}}
\] (7)

- This operator is **universal** ⇒ can be used for
  - the whole periodic table (and beyond)
  - all molecular geometries and assemblies (including transition states, fluids, solids, surfaces,...)

Ab-initio methods use this **universal** \( \hat{H} \) (and make “no” further approximations).

- \( \hat{H} \) is **fully specified by stating your molecular system**;
  this fixes \( N, K, \) and \( (M_A, Z_A) \) for all nuclei \( A \)

- \( \hat{H} \) contains **no chemical bonds** ⇒ bond information input is not necessary and **not possible**
  (getting bond information as output is not easy and not well-defined)

- \( \hat{H} \) contains **no association between nuclei and electrons** ⇒ you cannot input desired charge distributions, dipole moments, etc. (and: atomic charges as output are not well defined, see below)
**Born-Oppenheimer separation**

The time-indep. molecular Schrödinger eq. $\hat{H}_{mol}^{(k)} = \mathcal{E}_k \Psi_{mol}^{(k)}$ is easier to solve after separating it into

1. **one** electronic Schrödinger equation, for **fixed**, pre-defined nuclear coordinates $\mathbf{R}$:

$$\hat{H}_{el} \Psi^{(n)}(\mathbf{r}, \mathbf{R}) = E_n(\mathbf{R}) \Psi^{(n)}(\mathbf{r}, \mathbf{R})$$  \hspace{1cm} (8)

2. (infinitely) **many**, coupled nuclear Schrödinger equations:

$$[\hat{T}_N + E_m(\mathbf{R})] \chi^{(m,k)}(\mathbf{R}) + \sum_n [2\hat{T}'_{mn}(\mathbf{R}) + \hat{T}''_{mn}(\mathbf{R})] \chi^{(n,k)}(\mathbf{R}) = \mathcal{E}_k \chi^{(m,k)}(\mathbf{R})$$  \hspace{1cm} (9)

- This B.-O. separation is still **exact**!
- B.-O. approximation = neglect couplings $\hat{T}'$, $\hat{T}''$ between nuclear eqs.9
- additional input due to B.-O. separation: $\mathbf{R}$ = coordinates of all nuclei
- remainder of this course:
  - solve “only” eq.8
  - ignore eq.9

Some potential energy surfaces $E_m(\mathbf{R})$ of ICN as function of the I–CN distance
Many-electron wavefunction

Solving the electronic Schrödinger equation $\hat{H}_{el} \Psi^{(n)}(r) = E_n \Psi^{(n)}(r)$ for the unknown $E_n$ and $\Psi^{(n)}$ in full generality is too difficult, because $\Psi$ is very high-dimensional: $\Psi(r_1, r_2, \ldots, r_N) \Rightarrow 3N$-dimensional

**Simplifying approximation:** using much simpler (but yet unknown!) one-electron wavefunctions (called \textbf{orbitals}), restrict $\Psi$ to this functional form:

$$\Psi(r_1, r_2, \ldots, r_N) = \psi_k(r_1)\psi_\ell(r_2)\cdots\psi_m(r_N) \quad \text{"Hartree product"} \quad (10)$$

This induces (at least) these \textbf{two errors}:

1. electrons are \textbf{uncorrelated} (distributions of electron-$i$ and electron-$j$ are statistically \textit{independent})
2. we ignore that electrons are \textit{fermions}.

We fix error-2 by linear combinations of many Hartree products with correct sign changes:

$$\Psi(r_1, r_2, \ldots, r_N) = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc} \psi_i(r_1) & \psi_j(r_1) & \cdots & \psi_k(r_1) \\ \psi_i(r_2) & \psi_j(r_2) & \cdots & \psi_k(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_i(r_N) & \psi_j(r_N) & \cdots & \psi_k(r_N) \end{array} \right| \quad \text{"Slater determinant"} \quad (11)$$

This ensures antisymmetry of $\Psi$ upon label exchange of electrons (needed for fermions!):

$$\Psi(\ldots, r_i, \ldots, r_j, \ldots) = -\Psi(\ldots, r_j, \ldots, r_i, \ldots) \quad (12)$$

Note: error-1 remains \textbf{unfixed!} (for now)
...now finally solve the Schrödinger equation:

One can prove very generally that solving $\hat{H}\Psi = E\Psi$ is equivalent to finding extrema of $E = \langle \Psi | \hat{H} | \Psi \rangle$

⇒ **two possible strategies:** To determine $E$ and $\Psi$ simultaneously,

- we minimize $E = \langle \Psi | \hat{H} | \Psi \rangle$ or solve the Hartree-Fock eqs. $\hat{f}|\psi_m\rangle = \epsilon_m|\psi_m\rangle$
- by varying all orbitals $\psi$ in the Slater determinant $\Psi$.

**Technical details:**

- **iterative** procedure necessary in both cases (nonlinear optimization or SCF cycles)
- the optimal **orbitals are not unique:**

  arbitrary linear combinations of the orbitals leave everything of interest unchanged!
  ⇒ different sets of orbitals possible (canonical, natural, local,...)
  ⇒ arguments based on orbital shapes have to be viewed with caution!
Orbital variation made easy (1/2)

To vary the orbitals $\psi$, we expand them in known basis functions:

$$\psi(x) \approx \sum_{i=1}^{n} c_i \phi_i(x)$$  \hspace{1cm} (13)

This is similar to other series expansions we know:

**Taylor series**

$$\frac{1}{1+x} = 1 - x + x^2 - x^3 + x^4 - x^5 \pm \cdots$$

**Fourier series**

$$|\sin(x)| \approx \frac{2}{\pi} - \frac{4}{\pi} \left( \frac{1}{3} \cos(2x) + \frac{1}{15} \cos(4x) + \frac{1}{35} \cos(6x) \right)$$
Orbital variation made easy (2/2)

To vary the orbitals $\psi$, we expand them in known basis functions:

$$\psi(x) \approx \sum_{i=1}^{n} c_i \phi_i(x)$$  \hspace{1cm} (14)

- all $\phi_i$ are known $\Rightarrow$ variation of 1 function $\psi$ reduces to (linear) variations of $n$ numbers $c_i$
- in general, you can choose $\phi_i$ any way you want
- but in practice choose cleverly:
  - for fixed $n$, approximation in eq.14 improves if $\phi_i$ are more similar to target $\psi_{opt}$
  - if $n$ increases, approximation in eq.14 improves, but computer time increases (drastically)
  - $n \rightarrow \infty$ is impossible, large $n$ may be impractical

$\Rightarrow$ independent of errors due to the method (HF, DFT,\ldots)

= intrinsic error,

there also is a basis set error due to finite basis set

\[ 	ext{Fig. 15.2. The dependence of the calculated property on the quality of the basis.} \]
Basis sets (1/2)

Typically, in molecular calculations, pre-defined basis sets optimized by experts are used. **Recommendation:** correlation-consistent basis sets $\text{cc-pVnZ}$, with $n=\text{D,T,Q,5,6,\ldots}$

- **disadvantage:** $\text{cc-pVnZ}$ basis sets grow quickly with $n$
- **advantages:**
  - each function included in level $n$ is more important than each function left out
  - $\Rightarrow$ systematic basis set improvement possible *in practice*
  - fit to suitable function allows extrapolation to $n \to \infty = \text{complete basis set (CBS)}$

**Fig. 8.19.** The convergence of the MP2 correlation energy (full line) and the Hartree–Fock energy (dotted line) in meV for $\text{N}_2$ calculated using the $\text{cc-pCVXZ}$ basis sets. On the left, we have plotted the *correlation energies* superimposed on a fit of the form (8.4.3) with the horizontal axis representing the asymptotic limit of $-537$ meV. On the right, we have plotted the *errors in the correlation energy* superimposed on the fitted form (8.4.3) (full line) as well as the errors in the Hartree–Fock energy (dotted line) on a logarithmic scale.
Basis sets (2/2)

Typically, in solid-state calculations, plane-wave $e^{ikx}$ basis sets are used, characterized by a cutoff in frequency (energy) $\Rightarrow$ increase cutoff to convergence.

A molecular calculation with plane waves needs 25000–100000 basis functions. Compare to number of basis functions in molecular basis sets, e.g., for H$_2$O:

<table>
<thead>
<tr>
<th>basis set name</th>
<th># basis functions</th>
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<tbody>
<tr>
<td>3-21G</td>
<td>13</td>
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<tr>
<td>6-31G*</td>
<td>19</td>
</tr>
<tr>
<td>cc-pVDZ</td>
<td>24</td>
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<tr>
<td>cc-pVTZ</td>
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<tr>
<td>cc-pV6Z</td>
<td>322</td>
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<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Rightarrow$ ALL molecular basis sets are extremely small!

Important in practical calculations:

- never believe the result of a single calculation (one basis set size $n$)
- instead systematically increase basis set to reduce basis set error (or for CBS)
- adapt basis to situation, e.g., add “diffuse functions” (aug-) for negative ions and excited states
for $n$ basis functions, HF and DFT solve an $(n \times n)$ matrix eigenvalue problem
$\Rightarrow$ result: $n$ molecular orbitals, independent of the number $N$ of electrons

- the upper two thirds of the orbitals are crap!
  $\Rightarrow$ for $N$ electrons, we need at least $\frac{3}{2} N$ basis functions

- automatically o.k. in typical practice
  (unless you use extremely small basis sets like 3-21G)

- but HF and DFT also produce many virtual orbitals:
  - useful for explicit electron correlation
    (see below)
  - they are not part of the HF/DFT wavefunction, hence they are not really meaningful
    (despite Koopman’s theorem)
summary: a typical ab-initio calculation

To start a calculation, specify in the input (file):

- which molecule(s) you want (element symbols) \( \Rightarrow \) nuclear charges \( Z_A \)
- their structure(s) \( \Rightarrow \) nuclear coordinates \( R_A \)
- total charge and spin \( \Rightarrow \) number of electrons, orbital occupancy, spin state
- basis set (from given library)
- method (HF, DFT,...)

Start the program, wait for it to finish...,...find the result number(s) you want in the output.

What can go wrong?

- program bugs or crashes (highly unlikely; and remember: these programs are universal!)
- very many integrals over basis functions are needed \( \Rightarrow \) possibly insufficient memory and/or disk space
- iterative solution may fail to converge
- it simply takes too long (parallelizability is rather restricted)

If nothing goes wrong, you get an answer, but NO error estimate of any kind.

YOU have to judge if the result is o.k. or crap!
**Spin, closed/open shell**

Standard electronic-structure calculations produce eigenfunctions of the total electronic spin operator $\Rightarrow$ You have to specify initially the desired spin state.

To construct the proper spin state in more complicated cases, linear combinations of several Slater determinants are needed (configuration state function (CSF)).

Electron spin is treated via formal spin functions. Integration over products of spin functions yields 1 or 0 $\Rightarrow$ some of the basis function integrals disappear.

It turns out that this does not need to be re-done for each individual case, instead it only has to be done for these classes of systems:

![Energy level diagram](attachment:image.png)

**YOU** have to choose!

e.g., radicals cannot be calculated with RHF.
What is Density Functional Theory (DFT)?

The RHF energy expression is:

$$E_0 = 2 \sum_{m}^{N/2} h_{mm} + \sum_{m}^{N/2} \sum_{n}^{N/2} (2J_{mn} - K_{mn})$$

(15)

with the 1-electron integrals

$$h_{mm} = \int \psi_m^*(\mathbf{r}_1) \left( -\frac{1}{2} \nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) \psi_m(\mathbf{r}_1) d\mathbf{r}_1$$

(16)

and two types of 2-electron integrals: Coulomb integrals

$$J_{mn} := \int \int \psi_m^*(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_m(\mathbf{r}_1)\psi_n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \int \int |\psi_m(\mathbf{r}_1)|^2 \frac{1}{r_{12}} |\psi_n(\mathbf{r}_2)|^2 d\mathbf{r}_1 d\mathbf{r}_2$$

(17)

and exchange integrals:

$$K_{mn} := \int \int \psi_m^*(\mathbf{r}_1)\psi_n^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_n(\mathbf{r}_1)\psi_m(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

(18)

Note that the RHF energy in eq.15 is a functional of the orbitals $\psi_i$ and contains no electron correlation (ignoring Fermi correlation from antisymmetry).

Dropping HF exchange and inserting a new, different functional $E_{xc}$ that takes care of exchange and(!) correlation gives us (Kohn-Sham-)DFT. Unfortunately, the correct $E_{xc}$ is not known yet...
What is DFT not?

DFT is often advertised as being based on the 3-dimensional density (in(!)dependent of $N$)

$$\rho(r_1) = N \int \cdots \int |\Psi|^2 dr_2 \cdots dr_N$$

rather than on the 3N-dimensional wavefunction $\Psi(r_1, r_2, \ldots, r_N) = \text{big simplification!}$

In practice, this is not true!

All current end-user DFT is KS-DFT = contains orbitals and s.th. like $\Psi$ (cf. previous page).

Truly $\Psi$-independent DFT is now called “orbital-free DFT” (OF-DFT).

Historically, this was tried very early (1920s) and failed badly: all molecules dissociated into atoms.

Modern OF-DFT approaches reach accuracy levels of good force fields.

The Hohenberg-Kohn theorems are often cited as existence proofs for an exact $E_{xc}$. However,

- they are wavefunction-based and do not directly use any density arguments
- they merely show that specifying the “external potential” (positions and charges of all nuclei) and $N$ (number of electrons) uniquely determines the electronic wavefunction $\Psi$ (and hence $\rho$)
- $\Rightarrow \rho$ determines $(\hat{H}$ which determines $\Psi$ which determines) all molecular properties
- $\Rightarrow$ there is an exact density functional (if “functional” is defined sufficiently widely)

But all this gives us no clue how the exact functional or the exact $E_{xc}$ should look like.

50 years(!) after Hohenberg&Kohn we are still searching for it…
Current status of DFT

• HF is obsolete, DFT gives better results for similar computational cost
• basis set requirements modest (compared to explicit correlation): expect convergence at cc-pVTZ
• there are > 50 density functionals available; sorting attempt:

<table>
<thead>
<tr>
<th>Level</th>
<th>Name</th>
<th>Variables</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Local density</td>
<td>ρ</td>
<td>LDA, LSDA, Xα</td>
</tr>
<tr>
<td>2</td>
<td>GGA</td>
<td>ρ, ∇ρ</td>
<td>BLYP, OPTX, OLYP, PW86, PW91, PBE, HCTH</td>
</tr>
<tr>
<td>3</td>
<td>Meta-GGA</td>
<td>ρ, ∇ρ, ∇²ρ or τ</td>
<td>BR, B95, VSXC, PKZB, TPSS, τ-HCTH</td>
</tr>
<tr>
<td>4</td>
<td>Hyper-GGA</td>
<td>ρ, ∇ρ, ∇²ρ or τ</td>
<td>H+H, ACM, B3LYP, B3PW91, O3LYP, PBE0, TPSSh, τ-HCTH-hybrid</td>
</tr>
<tr>
<td>5</td>
<td>Generalized RPA</td>
<td>ρ, ∇ρ, ∇²ρ or τ</td>
<td>OEP2</td>
</tr>
</tbody>
</table>

Expectation: quality of results increases from level 1 to level 5, but system-dependent exceptions are to be expected!

• DFT is under constant development ⇒ today’s DFT problems (next page) may be solved soon…
DFT caveats

• electron self-interaction cancels out in HF but not in DFT; solutions are still a topic of current research (e.g.: http://dx.doi.org/10.1063/1.4869581)

• expect van-der-Waals interactions to be always incorrect! Solutions range from:
  – simple force-field corrections (DFT-D, DFT-D2, DFT-D3; Grimme)
  – via an extra term in the functional (vdW-DF’)
  – to ingredients from explicit correlation theory (RPA, TD-DFT)

(review: http://dx.doi.org/10.1063/1.4754130)

Much of that is available in standard program packages but needs to be “switched on”. Expect vdW contributions to be important e.g. for

  – conformational energies of larger molecules
  – molecular interactions in the gas phase (including “π-stacking”)
  – adsorption of molecules on surfaces
  – molecular crystals

• $\Psi_{DFT}$ is a single Slater determinant (just as in HF); expect DFT (and HF) to fail in multideterminantal/multireference situations:

  – dissociation of covalent bonds
  – near transition states (in the electronic ground state)
  – for many excited states (see below)
Explicit electron correlation methods

NOT treated here.

Necessary main ingredient: one Slater determinant $\rightarrow$ many Slater determinants

$$\Psi_{HF/DFT} = S[\{\psi_i\}] \rightarrow \Psi_{corr.} = \sum_{n} c_n S_n[\{\psi_i\}]$$ (20)

Many methods: MP2, MP4,\ldots, CI (with CISD etc.), CC (with CCSD, CCSD(T), etc.),\ldots

Practical rules of thumb for explicit correlation:

- huge computational expense
- size scaling much worse than for HF/DFT
- much larger basis sets needed (never do or believe a calculation like CCSD(T)/6-31G!)
  $\rightarrow$ even larger computational expense
- analytical gradients often not available (but too expensive anyway)
- limited availability for periodic (solid-state) calculations
- for small to mid-size molecules, MP2 may be less expensive than DFT
  $\Rightarrow$ do try MP2! Differences between MP2 and DFT results indicate problem cases.
- systems with multireference character are problematic even for standard versions of MPn, CI, CC,\ldots $\Rightarrow$ multireference versions needed: CASSCF/CASPT2, MRCI, MRCC,\ldots
Geometry optimization

B.-O. separation \(\Rightarrow\) molecular structure is \textit{required} input!

Normally, experimentally determined geometries differ (slightly) from theoretical ones \(\Rightarrow\) to get reasonable energies (and properties), you first need to \textit{optimize the geometry} of your system.

Working hypothesis: Stable molecular structures correspond to PES minima.
\(\Rightarrow\) Geometry optimization algorithm:

1. user supplies: arbitrary starting structure \(X_{\text{initial}}\), choice of method \(M\)
2. using method \(M\), calculate energy and gradient \(\partial E/\partial X\) at current structure \(X_i\)
3. change structure: \(X_{i+1} = X_i + \Delta X_i\), such that energy decreases (using info from gradient \(\partial E/\partial X\))

Figure 14.1 Steepest descent minimization
Geometry optimization algorithm:

1. user supplies: arbitrary starting structure $X_{initial}$, choice of method M
2. using method M, calculate energy and gradient $\partial E/\partial X$ at current structure $X_i$
3. change structure: $X_{i+1} = X_i + \Delta X_i$, such that energy decreases (using info from gradient $\partial E/\partial X$)
4. check for convergence (e.g., $X_{i+1} - X_i$, or $E_{i+1} - E_i$, or size of gradient; with default thresholds)
5. if not converged, go to (2)
6. else output final structure $X_{final}$

Since step (2) is expensive, most quantum-chemistry packages are very clever in step (3) $\Rightarrow$ quick convergence to minima can be expected (unless you use a bad program package).
Hints for using geometry optimization

- in practice, all PESs have multiple minima \( \Rightarrow X_{\text{final}} \) depends on \( X_{\text{initial}} \)
  \( \Rightarrow \) always check \( X_{\text{final}} \) visually! Possibly retry geometry optimization with different \( X_{\text{initial}} \)

- geometry optimization may converge to saddle points (b/c there gradient=0 is also true)
  \( \Rightarrow \) always check if \( X_{\text{final}} \) is a true minimum, by a frequency calculation (see below)

- DFT needs numerical integration \( \Rightarrow \) “numerical noise” may induce convergence problems or false minima in “shallow valleys”; solution: retry with finer DFT integration grid

- default convergence thresholds often sufficient, but may need to be tightened in certain cases (if in doubt, just try)

- numerical gradients \( \frac{\partial E}{\partial X} \approx \frac{\Delta E}{\Delta X} \) are always available, BUT always do geometry optimizations with methods that have analytical gradients implemented! (check package docu). Illustration:

  For aniline, a single-point DFT calculation may need 5 min.
  The analytical gradient needs another 5 min.
  For 14*3=42 degrees of freedom (DOF) and central differences (2 single-points per DOF), the numerical gradient needs 42*2*5 min = 420 min = 7 h.

- unless you are 100\% sure of what you are doing, avoid (accidental) symmetries in your starting geometry \( X_{\text{initial}} \)!
  Reason: The gradient has the same symmetry \( \Rightarrow \) unless helped by “numerical noise”, your system is stuck in this symmetry, but the true minimum may have a different (or no) symmetry...
2nd derivatives: frequencies (1/2)

2nd derivatives (Hessian) \( \frac{\partial^2 E}{\partial X^2} \)

- use *analytical* Hessian (even more important than for gradient)
- related to nuclear vibrations via *normal mode analysis*:
  - applicable **ONLY** at stationary points (minima, saddle points, maxima)
    \( \Rightarrow \) *always* do a well-converged geometry optimization beforehand!
  - uses quadratic approximation of potential, hence
    * valid only for small vibrational amplitudes
    * *all* results are harmonic (but all real vibrations are more or less anharmonic)
  - for \( N \) atoms, normal mode analysis yields
    * 3\( N \) eigenvalues; their square roots are the normal mode harmonic frequencies
    * 3\( N \) eigenvectors = contributions of the nuclear cartesian coordinates to each normal mode vibrational movement \( \Rightarrow \) easy visualization!

- electron correlation insufficient in HF and DFT
  \( \Rightarrow \) bond dissociation asymptotes too high in energy
  \( \Rightarrow \) frequencies systematically too high

- *anharmonic* frequency calculations: possible, many methods, but *computationally expensive!*
2nd derivatives: frequencies (2/2)

2nd derivatives are useful for

- checking stationary points:
  minimum = all frequencies real, 1st-order saddle point = 1 imaginary frequency
- zero-point vibrational energy correction
- vibrational frequencies are the only really difficult-to-obtain information in the molecular partition function ⇒ after a frequency calculation, you get statistical thermodynamics data “for free”
- IR/Raman spectra simulation
  - normal mode frequencies → peak positions
  - derivative of dipole (IR) or polarizability (Raman) w.r.t. nuclear coordinates → peak intensities
  - peak widths approximated by convolution with instrument function

Fig. 7.4 Experimental (gas phase), DFT (B3LYP/6-31G*) and ab initio (MP2/6-31G*) calculated IR spectra of acetone
Finding reaction paths

1. determine minimum-energy geometries for reactants and products
2. get crude approximation to transition-state (TS) geometry $X_{TS}$
   - by more or less clever computational interpolation (probably built-in)
   - and/or chemical intuition
3. start geometry optimization to refine to true $X_{TS}$ (may fail by running down into a minimum!)
1. determine minimum-energy geometries for reactants and products
2. get crude approximation to transition-state (TS) geometry $X_{TS}$
   - by more or less clever computational interpolation (probably built-in)
   - and/or chemical intuition
3. start geometry optimization to refine to true $X_{TS}$ (may fail by running down into a minimum!)
4. calculate & check frequencies at TS: exactly 1 imaginary freq?
5. change $X_{TS}$ by a non-small amount along this imaginary mode, in both directions (adding/subtracting this change) $\Rightarrow X^+, X^-$
6. for both $X^+, X^-$ as input geometries, start
   - a geometry optimization (towards minima)
   - or (if present) a reaction-path-following algorithm
7. check if the resulting end geometries
   - are true minima (no imaginary frequencies)
   - and are your initial reactant/product minima (step 1)

In practice, everything may succeed but end up in wrong minima in step 7. Then most likely s.th. went wrong in step 2; retry from there with better TS guess.

Depending on the program package, more or less of the above is automatized.
Molecular properties

Many properties can either be calculated from the molecular wavefunction $\Psi$ and the operator corresponding to the property, or from a suitable derivative of the energy; for example the dipole moment:

$$\mu = \langle \Psi | r | \Psi \rangle = -\frac{\partial E}{\partial F}$$

(21)

<table>
<thead>
<tr>
<th>$n_F$</th>
<th>$n_B$</th>
<th>$n_I$</th>
<th>$n_R$</th>
<th>Property</th>
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<td>Cotton–Mutton effect</td>
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</table>

F: electric field, B: magnetic field, I: nuclear spin, R: nuclear coordinates
Partial charges, bond orders

Although related to multipole moments (dipole, quadrupole, . . . ), charges of atoms in molecules are NOT uniquely defined, neither are bond orders (single, double, triple bonds).

Reason: Delimiting regions of space “belonging to an atom” or “between two atoms” is arbitrary!

⇒ calculating partial charges and bond orders from a molecular wavefunction is possible, but

- several different recipes exist, some are better than others, but none is “best” or “correct”
- NEVER mix/compare results from different recipes!

<table>
<thead>
<tr>
<th>Table 9.2 Atomic charges for oxygen in H₂O</th>
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<tbody>
<tr>
<td>Basis</td>
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<td>STO-3G</td>
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<td>3-21G</td>
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<td>6-31G(d,p)</td>
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<td>6-311G(2d,2p)</td>
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<td>6-311++G(2d,2p)</td>
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<td>cc-pVDZ</td>
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<td>cc-pVTZ</td>
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<td>cc-pVQZ</td>
</tr>
<tr>
<td>aug-cc-pVDZ</td>
</tr>
<tr>
<td>aug-cc-pVTZ</td>
</tr>
</tbody>
</table>
Incorporating solvent

Two different choices:

**continuum solvation models:** no molecular details; solvent = continuous polarizable material with given dielectric constant; typical energy contributions:

- (free) energy of generating a suitable hole in the solvent for the solute
- dispersion, repulsion and electrostatic interactions between solute and solvent

Typical method abbreviations: PCM (polarizable continuum model), COSMO (conductor-like screening model; = CPCM in Gaussian), COSMO-RS.

*Advantage:* Usage as simple as specifying a keyword and the desired solvent dielectric constant.

*Disadvantage:* Cannot describe discrete solvent-solute interactions, e.g., hydrogen bonds.

**explicit solvation:** include explicit solvent molecules into the calculation.

To avoid huge computational costs, QM/MM partitioning is frequently employed ( = ONIOM in Gaussian).

*Be careful:* Reliable results require some interaction parameter tuning and reference calculations ⇒ not quite black-box.

Of course, it is possible in principle to combine both approaches.
Electronically excited states: difficulties

HF and DFT calculations generate virtual (unfilled) orbitals. Why cannot we generate excited-state wavefunctions by promoting an electron from a filled orbital into a virtual one?

Figure 14.1  The singly excited state on the right may be qualitatively viewed as deriving from movement of an electron out of the ground-state HOMO into the indicated higher energy orbital (perhaps following absorption of a photon carrying the appropriate quantum of energy). Note, however, that the optimized orbitals of the ground state are at best approximations to those of the excited state.
Electronically excited states: minimal methods

o.k., so let’s (1) promote an electron and then (2) do an SCF calculation (HF or DFT) for the resulting electron configuration.

This also fails, for at least two reasons:

1. since the SCF calculation optimizes the orbitals, we will end up in the electronic ground state again (in most cases)

2. even in the remaining cases, the excited-state wavefunction will likely not be orthogonal to the ground-state wavefunction, b/c they result from two independent calculations (but all eigenfunctions of the electronic Hamiltonian have to be orthogonal to each other)

Remedy for (2) (and silently avoiding (1)): configuration interaction singles (CIS)

- essentially “only” orthogonalizes all “singly excited Slater determinants” to each other and to the ground state
- w/o optimizing any orbitals: They remain the optimal ones for the HF ground(!) state.

Obviously, results will not be very good, but at least the calculation is possible and not obviously formally wrong ;-)
Electronically excited states: somewhat better methods

Further improvements over CIS:

• do not use HF orbitals for CIS, but instead use semiempirical orbitals specifically optimized for this purpose \( \rightarrow \) INDO/S, ZINDO,\ldots

• do not use HF orbitals for CIS, but instead DFT orbitals and the usual density functionals for the orbital integrals \( \rightarrow \) (Tamm-Dancoff approximation to) linear-response-time-dependent DFT (LR-TD-DFT/TDA)

Notes on TDDFT:

• TD-DFT itself is much more: DFT applied to the time-dependent Schrödinger equation \( \Rightarrow \) simulations of arbitrary dynamics

• LR-TD-DFT is a calculational short-cut to a special application of TDDFT:
  – first-order term in a Taylor series of the ground-state density response to an oscillatory perturbation
  – require this to solve the TD-DFT-Schrödinger equation
  – \( \Rightarrow \) eigenvalue equation for the poles of the response function

(TDDFT in quantum-chemistry packages usually is LR-TDDFT)

• do not be confused by the many weird abbreviations in this area (LR-TD-HF is often called “random phase approximation (RPA)”)
Abstract relation between excitations and time-dependence

If we have all stationary system eigenstates $\psi_n(x)$, from solving

$$\hat{H}\psi_n(x) = E_n\psi_n(x), \quad (22)$$

we can expand the general solution

$$\Psi(x, t) = e^{-i\hat{H}t/\hbar}\Psi(x, 0) \quad (23)$$

of the time-dependent Schrödinger equation

$$i\hbar\frac{\partial \Psi}{\partial t} = \hat{H}\Psi \quad (24)$$

into the complete set of $\{\psi_n\}$:

$$\Psi(x, t) = \sum_n c_n e^{-iE_nt/\hbar}\psi_n(x) \quad (25)$$

showing that

- the full time evolution is contained in the stationary eigenstates (and their eigenvalues)
- conversely, every (non-trivial) time evolution $\Psi(x, t)$ generally contains information on (all) eigenstates, even if $\Psi(x, 0)$ (before the start of a perturbation) is the stationary ground state.
- this is the only reason for “TD” in LR-TDDFT
  (TDDFT contains NO attempt to describe anything like dynamics of the electronic excitation process!)
Electronically excited states: the really good methods

- FCI/CBS: provably exact but practically impossible for molecules with > 2–3 atoms
- MR-CC: possibly very good but still under development
- MR-CI: not size-extensive/consistent, expensive, not-black-box
- CASSCF/CASPT2: expensive, not-black-box
- CI: expensive, not size-extensive/consistent, single-reference
- ...
- ⟨several methods under development, e.g. DMRG⟩
- ...

⇒ LR-TDDFT is popular not because it has the best theoretical foundation but largely because

- lack of better alternatives in practice,
- DFT is so popular.
LR-TD-DFT goodies and caveats

With LR-TD-DFT, in most quantum-chemistry packages you can now

- optimize excited-state geometries
- calculate excited-state properties

BUT always remember that LR-TD-DFT has problems

- at conical intersections (fundamental, not really solved yet)
- with Rydberg states (wrong functional asymptotics $\rightarrow$ wrong energies relative to valence excitations; improvements have been proposed but are not in general use)
- with charge-transfer states (wrong functional asymptotics again; alleviated by range-separated hybrid functionals: “short range: DFT, long range: HF”)
- with states containing significant double, triple,$\ldots$excitation character (LR-TDDFT/TDA contains only single excitations, just as CIS; can be repaired only by extending or avoiding very fundamental ingredients of TD-DFT)

All of these occur more frequently for higher excitation energies. $\Rightarrow$ basic rule of thumb:
Expect LR-TDDFT to be good for low excitation energies ($< -\epsilon_{HOMO}$) and to significantly degrade for higher excitation energies (wrong energy differences or even wrong state ordering).
Beyond LR-TD-DFT but still DFT

Most of the above problems of LR-TD-DFT can be fixed at higher levels of DFT theory, e.g.:

- spin-restricted ensemble-referenced Kohn-Sham (REKS): similar to CAS methods, fractional occupation numbers ⇒ restricted capabilities but still fairly cheap

- DFT/MRCI: better but more expensive, no analytical gradients

Status: still in development...
UV/vis spectra

CIS, ZINDO, LR-TDDFT for UV/vis “stick” spectra:

- response function poles = excitation energies/wavelengths → “stick positions”
- oscillator strengths $\sim \langle \Psi_0 | \mathbf{r} | \Psi_i \rangle$ → “stick heights”
- convolution with instrument function

**BUT** this involves only *one* molecular structure (usually the minimum-energy structure).

More realistic UV/vis spectra: ground-state *molecular dynamics* with periodic excited-state calculations: