분자 구조 계산 II. 에너지 계산 응용

KAIST 화학과

이윤섭

- 들뜬 상태 계산
- One-electron properties
- 일반 물성 계산
- 자유에너지 계산
- Multi-level protocols

A review paper containing many aspects of excited state calculations. And Machine Learning

Machine Learning for Electronically Excited States of Molecules
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and Philipp Marquetand*

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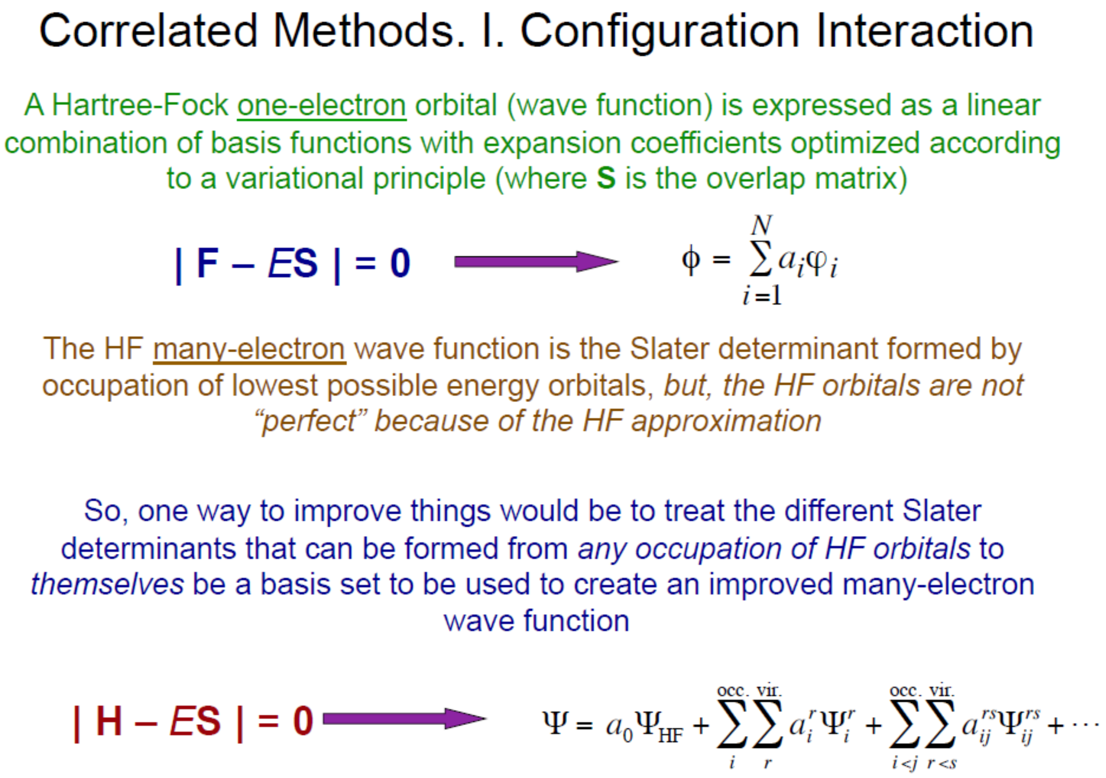
Abstract

Electronically excited states of molecules are at the heart of photochemistry, photophysics, as well as photobiology and also play a role in material science. Their theoretical description requires highly accurate quantum chemical calculations, which are computationally expensive. In this review, we focus on not only how machine learning is employed to speed up such excited-state simulations but also how this branch of artificial intelligence can be used to advance this exciting research field in all its aspects. Discussed applications of machine learning for excited states include excited-state dynamics simulations, static calculations of absorption spectra, as well as many others. In order to put these studies into context, we discuss the promises and pitfalls of the involved machine learning techniques. Since the latter are mostly based on quantum chemistry calculations, we also provide a short introduction into excited-state electronic structure methods and approaches for nonadiabatic dynamics simulations and describe tricks and problems when using them in machine learning for excited states of molecules

Excited Electronic States

- We usually write the Schrödinger equation as
$$H\Psi = E\Psi$$
- However, that obscures the reality that there are infinitely many solutions to the Schrödinger equation, so it is better to write
$$H\Psi_n = E_n\Psi_n$$
- Hartree-Fock theory provides us a prescription to construct an approximate ground-state wave function (as a single Slater determinant)
- How do we build from there to construct an excited-state wave function?

Excited States from Configuration Interaction (CI) Methods



Correlated Methods. I. Configuration Interaction

A Hartree-Fock one-electron orbital (wave function) is expressed as a linear combination of basis functions with expansion coefficients optimized according to a variational principle (where **S** is the overlap matrix)

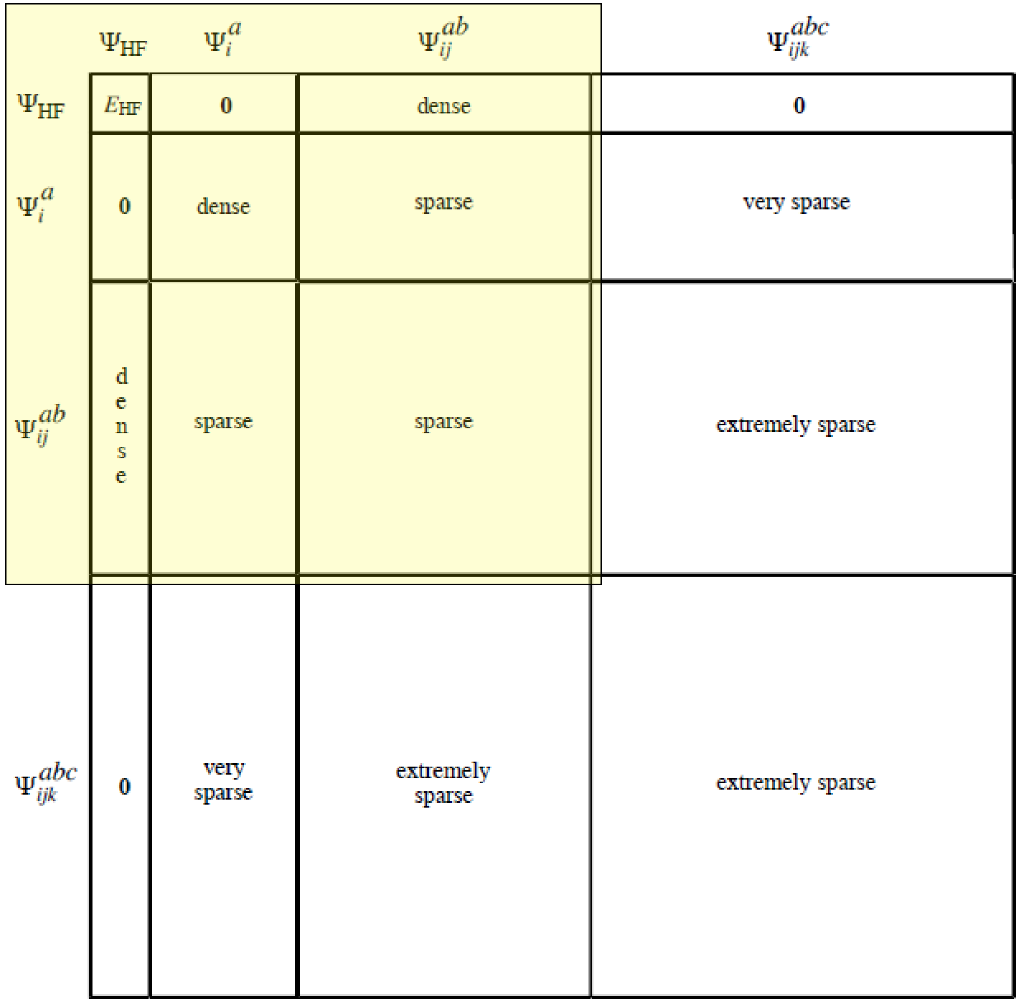
$$|\mathbf{F} - E\mathbf{S}| = 0 \longrightarrow \phi = \sum_{i=1}^{N} a_i \varphi_i$$

The HF many-electron wave function is the Slater determinant formed by occupation of lowest possible energy orbitals, *but, the HF orbitals are not "perfect" because of the HF approximation*

So, one way to improve things would be to treat the different Slater determinants that can be formed from *any occupation of HF orbitals* to *themselves* be a basis set to be used to create an improved many-electron wave function

$$|\mathbf{H} - E\mathbf{S}| = 0 \longrightarrow \Psi = a_0 \Psi_{\mathrm{HF}} + \sum_{i}^{\text{occ.}} \sum_{r}^{\text{vir.}} a_i^r \Psi_i^r + \sum_{i<j}^{\text{occ.}} \sum_{r<s}^{\text{vir.}} a_{ij}^{rs} \Psi_{ij}^{rs} + \cdots$$

CI in a Nutshell



	Ψ_{HF}	Ψ_i^a	Ψ_{ij}^{ab}	Ψ_{ijk}^{abc}
Ψ_{HF}	E_{HF}	0	dense	0
Ψ_i^a	0	dense	sparse	very sparse
Ψ_{ij}^{ab}	dense	sparse	sparse	extremely sparse
Ψ_{ijk}^{abc}	0	very sparse	extremely sparse	extremely sparse

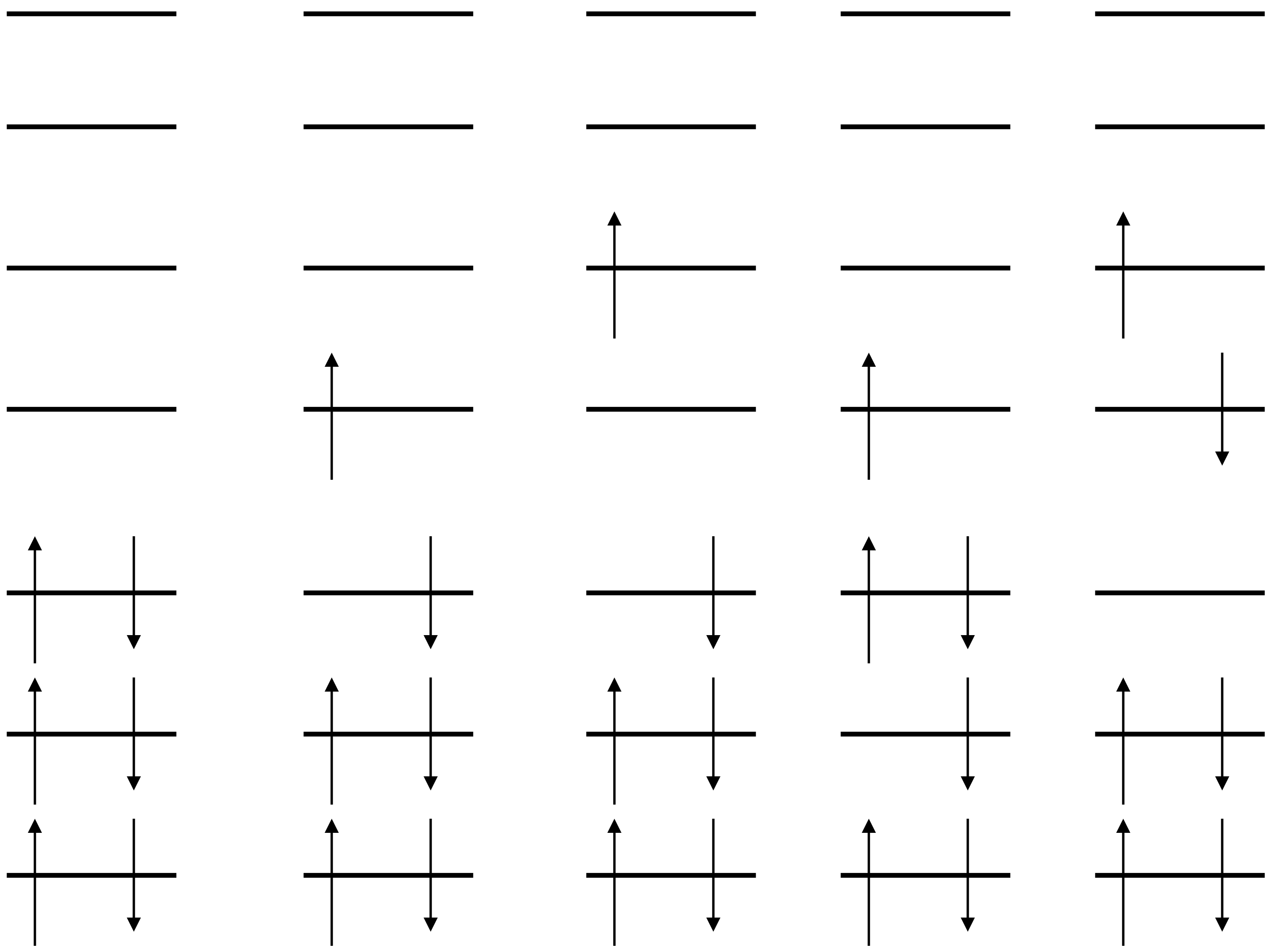
The bigger the CI matrix, the more electron correlation can be captured.

The CI matrix can be made bigger either by increasing basis-set size (each block is then bigger) or by adding more highly excited configurations (more blocks).

The ranked eigenvalues correspond to the electronic state energies.

Most common compromise is to include only single and, to lower ground state, double excitations (CISD)—not size extensive.

Ground State and Excited Configurations



ground state singly excited configurations double excitation

CI Singles (CIS)

$$\begin{array}{c|c|c|}
 & \Psi_{\mathrm{HF}} & \Psi_i^a \\
\hline
\Psi_{\mathrm{HF}} & E_{\mathrm{HF}} & \mathbf{0} \\
\hline
\Psi_i^a & \mathbf{0} & \text{dense} \\
\hline
\end{array}$$

There are *m* x *n* singly excited configurations where *m* and *n* are the number of occupied and virtual orbitals, respectively.

Diagonalization gives excited-state energies *and* eigenvectors containing weights of singly excited determinants in the pure excited state

Quality of excited-state wave functions about that of HF for ground state.

Efficient, permits geometry optimization; semiempirical levels (INDO/S) optimized for CIS method.

Koopmans' theorem

- orbital energy of an occupied orbital is approximately equal to the minus the ionization potential of that orbital

  IP of $\phi_i = \varepsilon_i$

- can be derived from the Hartree-Fock energy expression, if one assumes that the orbitals do not relax after ionization
- in a similar spirit, one can approximate the excitation energy

$$E(\Psi_i^a) - E(\Psi_0) = \varepsilon_a - \varepsilon_i$$

$$E(\Psi_{ij}^{ab}) - E(\Psi_0) = \varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j$$

Singlet vs Triplet States

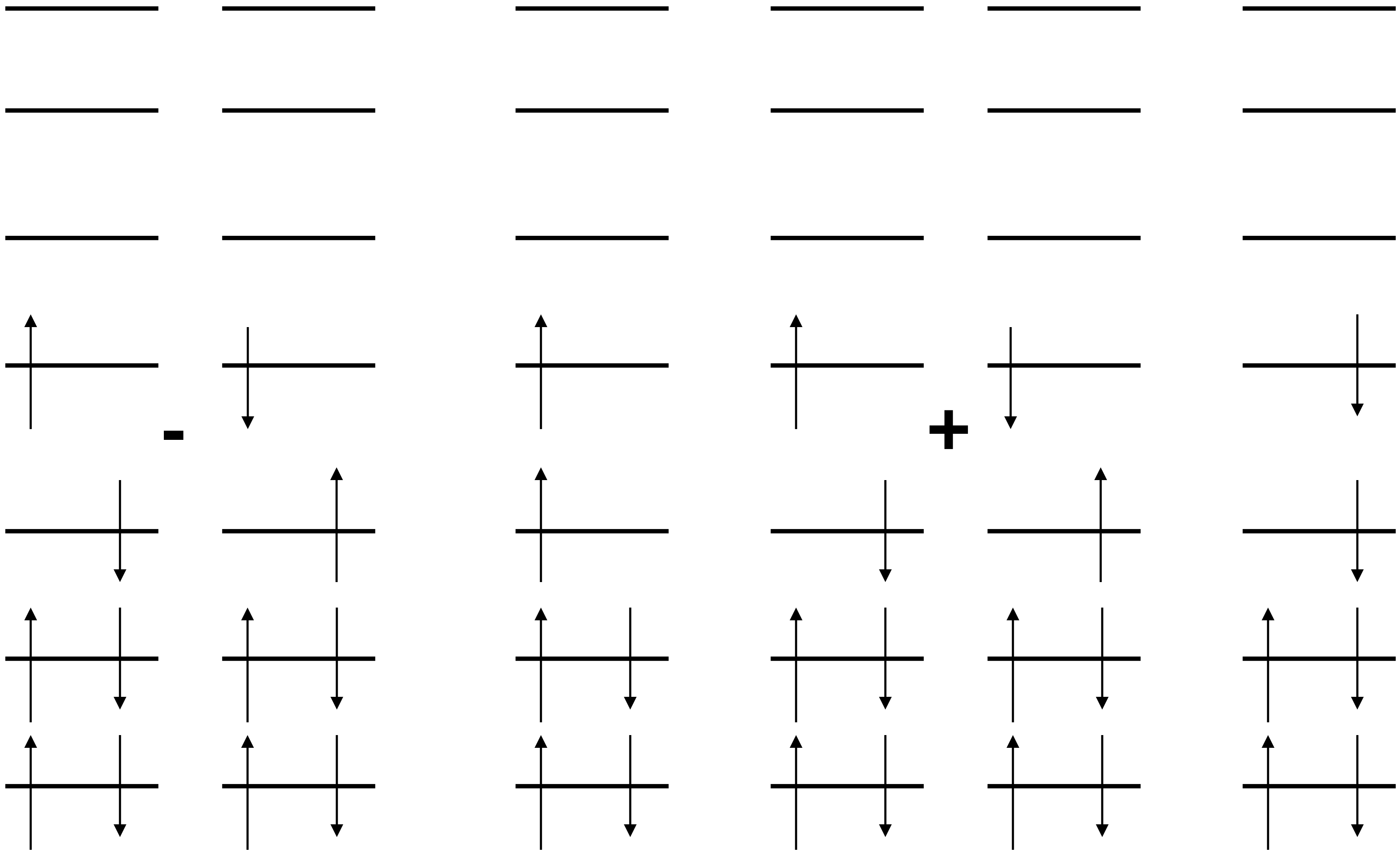
- Pauli principle says that the wavefunction must be antisymmetric, $\Psi(1,2)=-\Psi(2,1)$
- wavefunction is composed of space and spin parts
- if the space part is symmetric, then the spin part must be antisymmetric
- only one way to do this, singlet spin state
  - $[\alpha(1)\beta(2)-\beta(1)\alpha(2)]/2^{1/2}$

if the space part is antisymmetric, then the spin part must be symmetric

- three ways to do this, triplet spin state
  - $\alpha(1)\alpha(2)$
  - $[\alpha(1)\beta(2)+\beta(1)\alpha(2)]/2^{1/2}$
  - $\beta(1)\beta(2)$

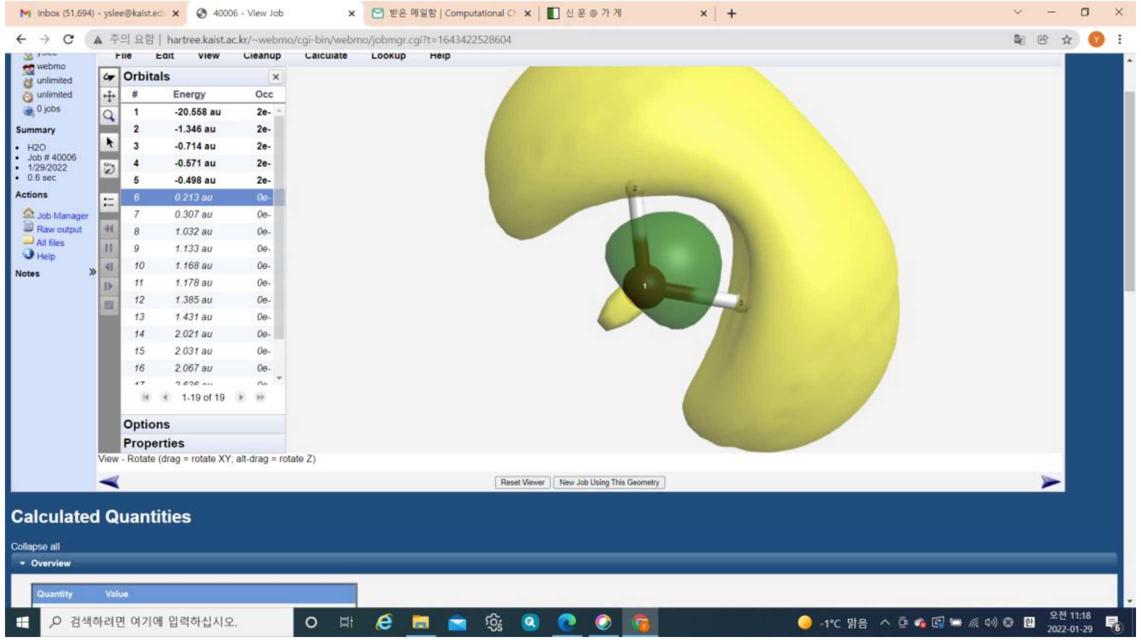
Singlet

. Triplet state .



$[\alpha(1)\beta(2)-\beta(1)\alpha(2)]/2^{1/2}$ $\alpha(1)\alpha(2)$ $[\alpha(1)\beta(2)+\beta(1)\alpha(2)]/2^{1/2}$ $\beta(1)\beta(2)$

Two low-lying virtual (unoccupied) orbitals of H_2O



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Summary

- H2O
- Job # 40006
- 1/29/2022
- 0.6 sec

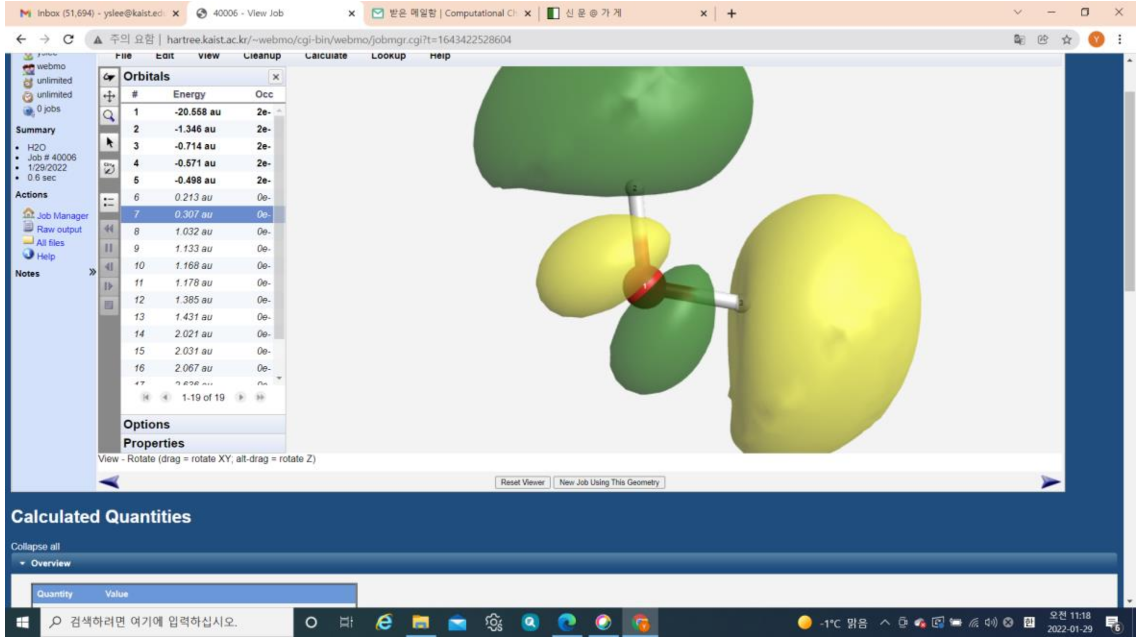
Orbitals

#	Energy	Occ
1	-20.558 au	2e-
2	-1.346 au	2e-
3	-0.714 au	2e-
4	-0.571 au	2e-
5	-0.498 au	2e-
6	0.213 au	0e-
7	0.307 au	0e-
8	1.032 au	0e-
9	1.133 au	0e-
10	1.168 au	0e-
11	1.178 au	0e-
12	1.385 au	0e-
13	1.431 au	0e-
14	2.021 au	0e-
15	2.031 au	0e-
16	2.067 au	0e-

1-19 of 19

View - Rotate (drag = rotate XY; alt-drag = rotate Z)

Calculated Quantities



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1-19 of 19

View - Rotate (drag = rotate XY; alt-drag = rotate Z)

Calculated Quantities

Δ SCF

- allow orbitals to relax, by doing a Hartree-Fock calculation on the excited state as well as on the ground state
- only works if excited state different symmetry than ground state (otherwise the attempt at calculating the excited state collapses to the ground state)
- OK for UHF calculation of the lowest triplet (since the number of alpha and beta spin electrons is different than in the ground state)
- possible (but tricky) for an excited singlet or triplet if the orbitals differ in symmetry
- in general, need to use configuration interaction

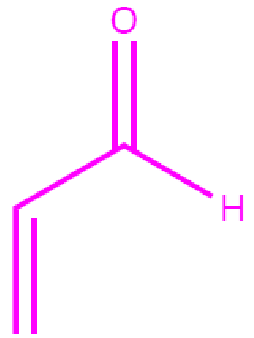
CI Singles (CIS) — Acrolein Example

```
Excited State   1:   Singlet-A"     4.8437 eV  255.97 nm  f=0.0002
      14 -> 16         0.62380        3.0329       408.79
      14 -> 17         0.30035        3.73

Excited State   2:   Singlet-A'     7.6062 eV  163.01 nm  f=0.7397
      15 -> 16         0.68354       6.0794       203.94
                                     6.41

Excited State   3:   Singlet-A"     9.1827 eV  135.02 nm  f=0.0004
      11 -> 16        -0.15957        6.6993       185.07
      12 -> 16         0.55680
      14 -> 16        -0.19752
      14 -> 17         0.29331

Excited State   4:   Singlet-A"     9.7329 eV  127.39 nm  f=0.0007
       9 -> 17        0.19146
      10 -> 16         0.12993
      11 -> 16         0.56876
      12 -> 16         0.26026
      12 -> 17        -0.11839
      14 -> 17        -0.12343
```



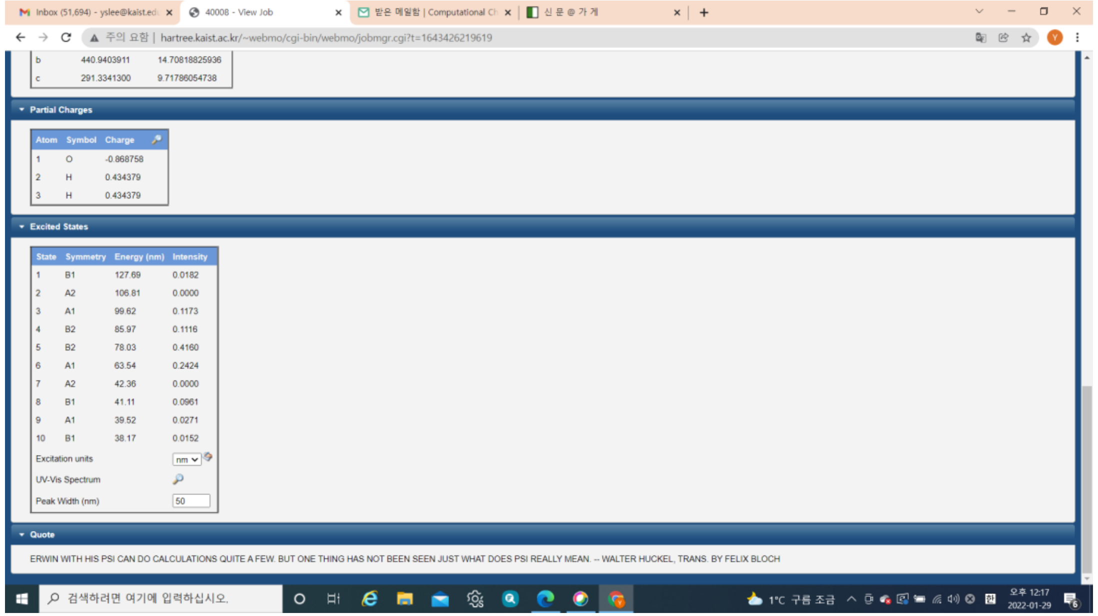
LUMO+1: π_4^*
LUMO: π_3^*
HOMO: π_2
HOMO–1: n_O

Expt

Eigenvectors CIS/6-31G(d) and INDO/S

CIS excitation energies too large, INDO better!

CIS calculation -> UV-VIS spectra



b	440.9403911	14.70818825936
c	291.3341300	9.71786054738

Partial Charges

Atom	Symbol	Charge
1	O	-0.868758
2	H	0.434379
3	H	0.434379

Excited States

State	Symmetry	Energy (nm)	Intensity
1	B1	127.69	0.0182
2	A2	106.81	0.0000
3	A1	99.62	0.1173
4	B2	85.97	0.1116
5	B2	78.03	0.4160
6	A1	63.54	0.2424
7	A2	42.36	0.0000
8	B1	41.11	0.0961
9	A1	39.52	0.0271
10	B1	38.17	0.0152

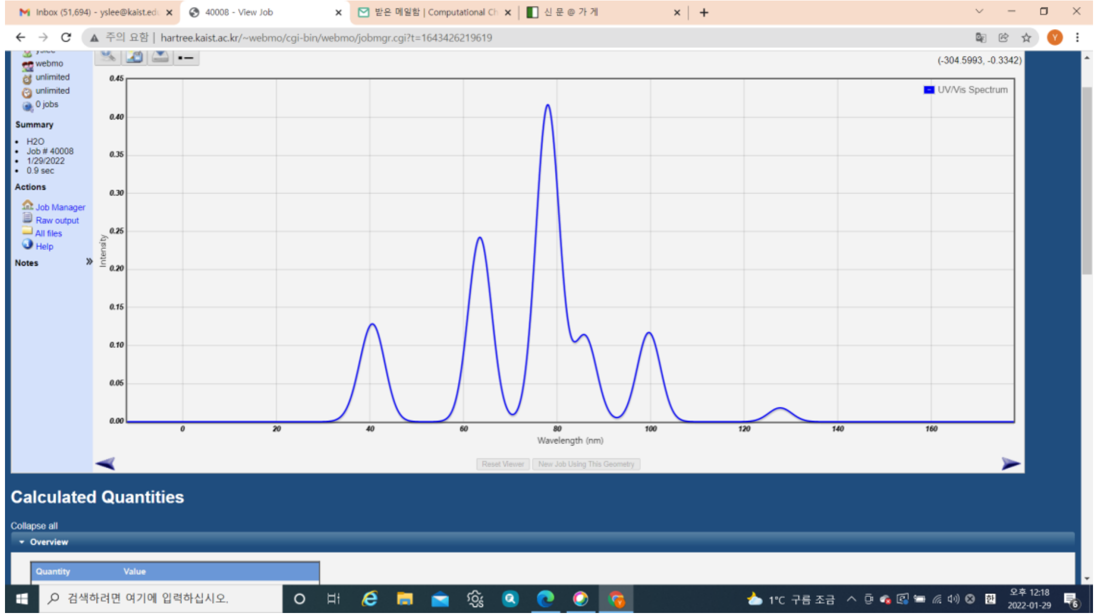
Excitation units: nm

UV-Vis Spectrum

Peak Width (nm): 50

Quote

ERWIN WITH HIS PSI CAN DO CALCULATIONS QUITE A FEW. BUT ONE THING HAS NOT BEEN SEEN JUST WHAT DOES PSI REALLY MEAN. -- WALTER HUCKEL, TRANS. BY FELIX BLOCH



Summary
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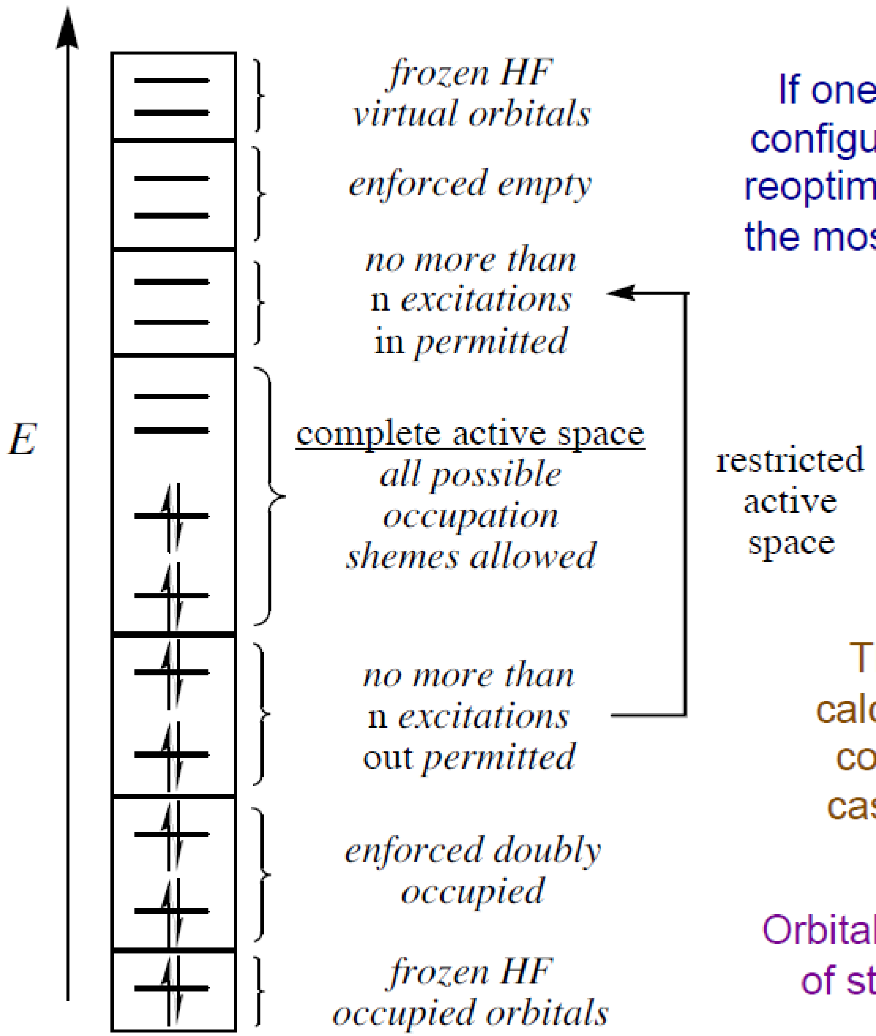
Calculated Quantities

This partitioning of orbital space useful to obtain excited states with electron correlations included

CI: Thème et Variation



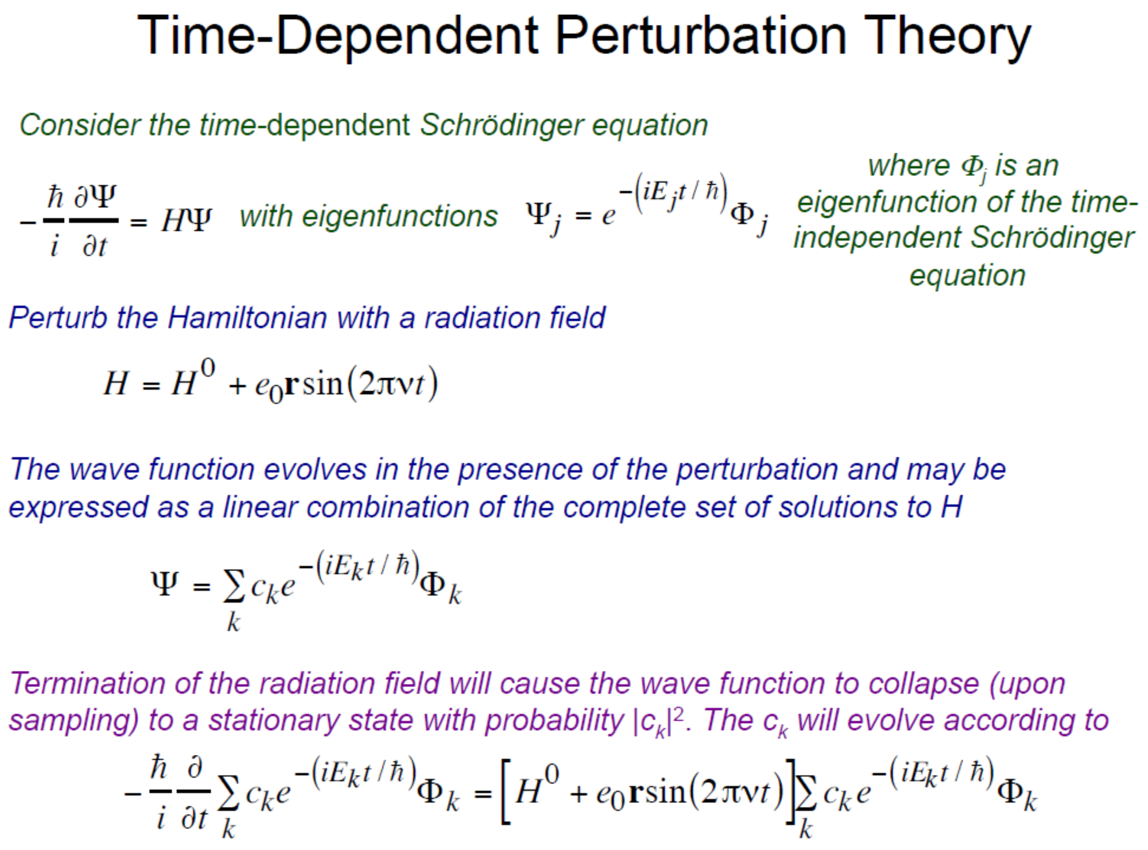
If one chooses not to include *all* excited configurations (full CI) perhaps one should reoptimize the basis-function coefficients of the most important orbitals instead of using their HF values

Maybe *more* excitations into lower-energy orbitals is a better option than *any* excitations into higher-energy orbitals

The general term for this class of calculations is multiconfiguration self-consistent field (MCSCF)—special cases are CASSCF and RASSCF—**CASPT2** adds accuracy

Orbital optimization can be for an average of state energies so as not to bias the orbitals to any one state

Transition to Excited States from Perturbation Theory and DFT



Time-Dependent Perturbation Theory

Consider the time-dependent Schrödinger equation

$$-\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = H\Psi$$

with eigenfunctions

$$\Psi_j = e^{-(iE_j t/\hbar)}\Phi_j$$

where Φ_j is an eigenfunction of the time-independent Schrödinger equation

Perturb the Hamiltonian with a radiation field

$$H = H^0 + e_0 \mathbf{r} \sin(2\pi\nu t)$$

The wave function evolves in the presence of the perturbation and may be expressed as a linear combination of the complete set of solutions to H

$$\Psi = \sum_k c_k e^{-(iE_k t/\hbar)}\Phi_k$$

Termination of the radiation field will cause the wave function to collapse (upon sampling) to a stationary state with probability $|c_k|^2$. The c_k will evolve according to

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\sum_k c_k e^{-(iE_k t/\hbar)}\Phi_k = \left[H^0 + e_0 \mathbf{r} \sin(2\pi\nu t)\right]\sum_k c_k e^{-(iE_k t/\hbar)}\Phi_k$$

Time-Dependent Perturbation Theory (cont.)

$$-\frac{\hbar}{i}\frac{\partial}{\partial t}\sum_k c_k e^{-(iE_k t/\hbar)}\Phi_k = \left[H^0 + e_0\mathbf{r}\sin(2\pi\nu t)\right]\sum_k c_k e^{-(iE_k t/\hbar)}\Phi_k$$

Taking the time derivative on the left and expanding on the right

$$-\frac{\hbar}{i}\sum_k \frac{\partial c_k}{\partial t} e^{-(iE_k t/\hbar)}\Phi_k + \sum_k c_k E_k e^{-(iE_k t/\hbar)}\Phi_k$$

$$= \sum_k c_k E_k e^{-(iE_k t/\hbar)}\Phi_k + e_0\mathbf{r}\sin(2\pi\nu t)\sum_k c_k e^{-(iE_k t/\hbar)}\Phi_k$$

Which simplifies to

$$-\frac{\hbar}{i}\sum_k \frac{\partial c_k}{\partial t} e^{-(iE_k t/\hbar)}\Phi_k = e_0\mathbf{r}\sin(2\pi\nu t)\sum_k c_k e^{-(iE_k t/\hbar)}\Phi_k$$

Left multiplication by state of interest and integration yields

$$-\frac{\hbar}{i}\sum_k \frac{\partial c_k}{\partial t} e^{-(iE_k t/\hbar)}\delta_{mk} = e_0\sin(2\pi\nu t)\sum_k c_k e^{-(iE_k t/\hbar)}\langle\Phi_m|\mathbf{r}|\Phi_k\rangle$$

Time-Dependent Perturbation Theory (cont.)

$$-\frac{\hbar}{i}\sum_k \frac{\partial c_k}{\partial t} e^{-(iE_k t/\hbar)}\delta_{mk} = e_0 \sin(2\pi\nu t)\sum_k c_k e^{-(iE_k t/\hbar)}\langle\Phi_m|\mathbf{r}|\Phi_k\rangle$$

Evaluate Kronecker delta, rearrange, and assume perturbation is small, so ground *state can be used for right-hand-side coefficients*

$$\frac{\partial c_m}{\partial t} = -\frac{i}{\hbar} e_0 \sin(2\pi\nu t) e^{-[i(E_m - E_0)t/\hbar]}\langle\Phi_m|\mathbf{r}|\Phi_0\rangle$$

Integrating over time of perturbation

$$c_m(\tau) = -\frac{i}{\hbar} e_0 \int_0^\tau \sin(2\pi\nu t) e^{-[i(E_m - E_0)t/\hbar]}\langle\Phi_m|\mathbf{r}|\Phi_0\rangle dt$$

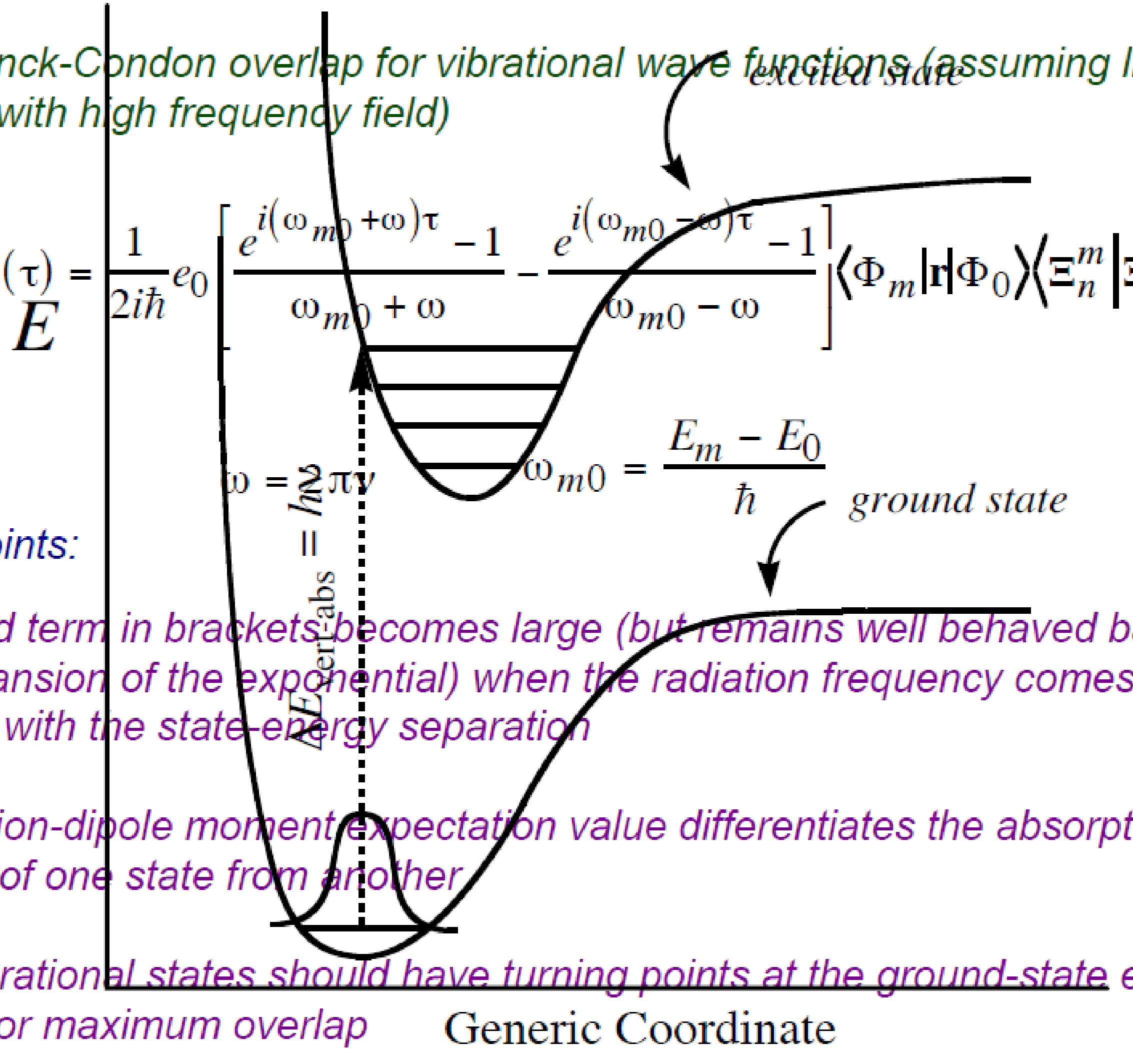
$$= \frac{1}{2i\hbar} e_0 \left[\frac{e^{i(\omega_{m0}+\omega)\tau} - 1}{\omega_{m0}+\omega} - \frac{e^{i(\omega_{m0}-\omega)\tau} - 1}{\omega_{m0}-\omega}\right]\langle\Phi_m|\mathbf{r}|\Phi_0\rangle$$

where

$$\omega = 2\pi\nu \qquad \omega_{m0} = \frac{E_m - E_0}{\hbar}$$

Time-Dependent Perturbation Theory (cont.)

Adding Franck-Condon overlap for vibrational wave functions (assuming little interaction with high frequency field)



$$c_{m,n}(\tau) = \frac{1}{2i\hbar} e_0 \left[\frac{e^{i(\omega_{m0}+\omega)\tau} - 1}{\omega_{m0}+\omega} - \frac{e^{i(\omega_{m0}-\omega)\tau} - 1}{\omega_{m0}-\omega} \right] \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle \langle \Xi_n^m | \Xi_0^0 \rangle$$

$$\omega = 2\pi\nu \qquad \omega_{m0} = \frac{E_m - E_0}{\hbar}$$

Qualitative points:

The second term in brackets becomes large (but remains well behaved based on series expansion of the exponential) when the radiation frequency comes into resonance with the state-energy separation

The transition-dipole moment expectation value differentiates the absorption probability of one state from another

Excited vibrational states should have turning points at the ground-state equilibrium geometry for maximum overlap

Time-Dependent Density Functional Theory

A similar mathematical formalism applied to density functional theory shows that excitation energies can be determined as poles of the polarizability matrix

$$\langle \alpha \rangle_{\omega} = \sum_{m>0} \left[\frac{\left| \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle \right|^2}{\omega_{m0} + \omega} \pm \frac{\left| \langle \Phi_m | \mathbf{r} | \Phi_0 \rangle \right|^2}{\omega_{m0} - \omega} \right]$$

$$\omega = 2\pi\nu \qquad \omega_{m0} = \frac{E_m - E_0}{\hbar}$$

Qualitative points:

TD DFT tends to be more accurate than CIS but this is sensitive to choice of functional and certain special situations

Charge-transfer transitions are particularly problematic

No wave function is created, but eigenvectors analogous to those predicted by CIS are provided

CI Singles (CIS) — Acrolein Example

```
Excited State   1:   Singlet-A"     4.8437 eV  255.97 nm  f=0.0002
     14 -> 16         0.62380        3.0329       408.79
     14 -> 17         0.30035        3.73

Excited State   2:   Singlet-A'     7.6062 eV  163.01 nm  f=0.7397
     15 -> 16         0.68354       6.0794       203.94
                                     6.41

Excited State   3:   Singlet-A"     9.1827 eV  135.02 nm  f=0.0004
     11 -> 16        -0.15957        6.6993       185.07
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Excited State   4:   Singlet-A"     9.7329 eV  127.39 nm  f=0.0007
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```
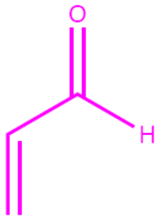

Eigenvectors CIS/6-31G(d) and INDO/S



LUMO+1: π_4^*
LUMO: π_3^*
HOMO: π_2
HOMO–1: n_O

Expt

- **TD-DFT**: PBE/6-31G(d)

(For DFT HOMO n_0 and HOMO-1 π_2)

- Ex. St. 1: ^{1}A” 3.7 eV
  - 15-> 16 0.62
  - 15-> 17 0.10
- Ex. St. 2: ^{1}A’ 6.6 eV
  - 14->16 0.60
  - 14->17 0.12
- Ex. St. 3: ^{1}A” 7.27 eV
- Ex. St. 4: ^{1}A” 7.70 eV

QC methods used for excited states in recent literature

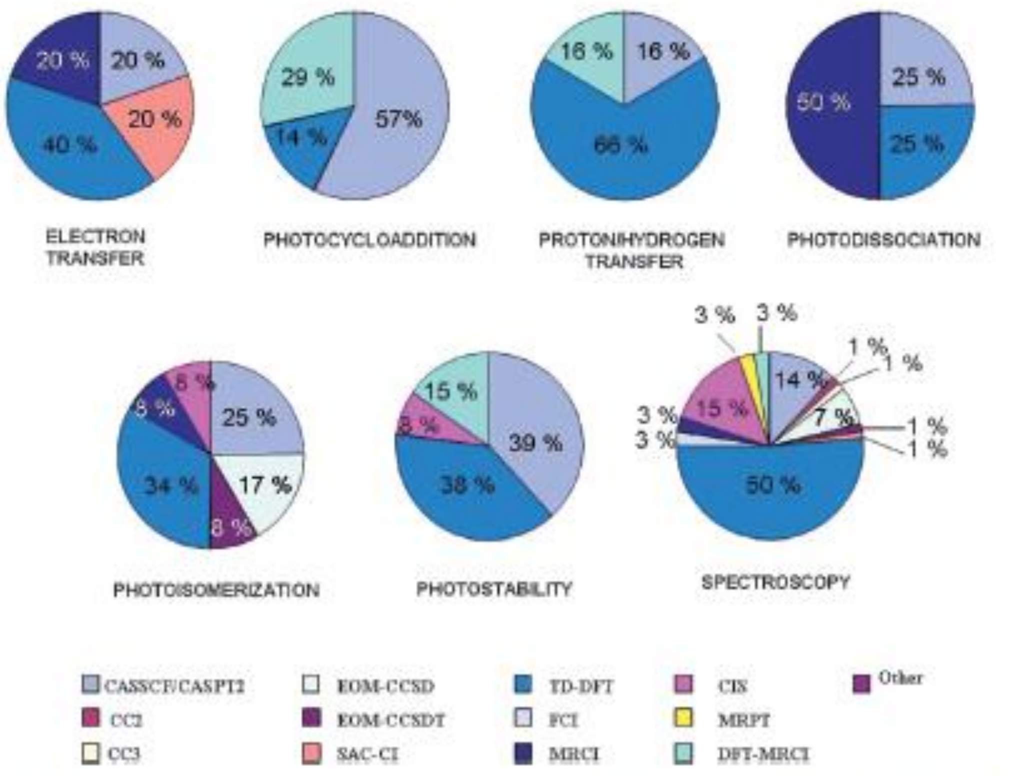


Figure 2. Studies found in the literature on molecular processes taking place in the excited state distributed by the different quantum chemical methods employed. The search parameters were "excited states" and "quantum chemistry" in the period 2007–2010. 106 papers are considered.[122]

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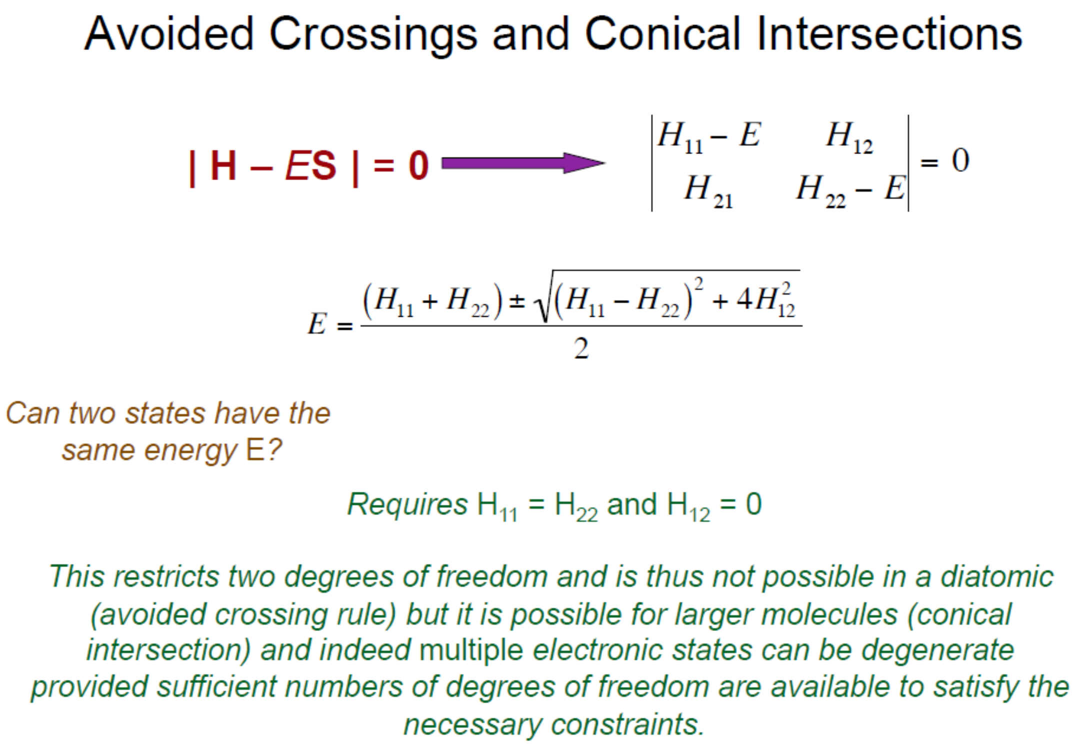
Gonzales et al.

Excited electronic states: Conical Intersections and Dynamics



Avoided Crossings and Conical Intersections

$$|\mathbf{H} - E\mathbf{S}| = 0 \longrightarrow \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

$$E = \frac{(H_{11} + H_{22}) \pm \sqrt{(H_{11} - H_{22})^2 + 4H_{12}^2}}{2}$$

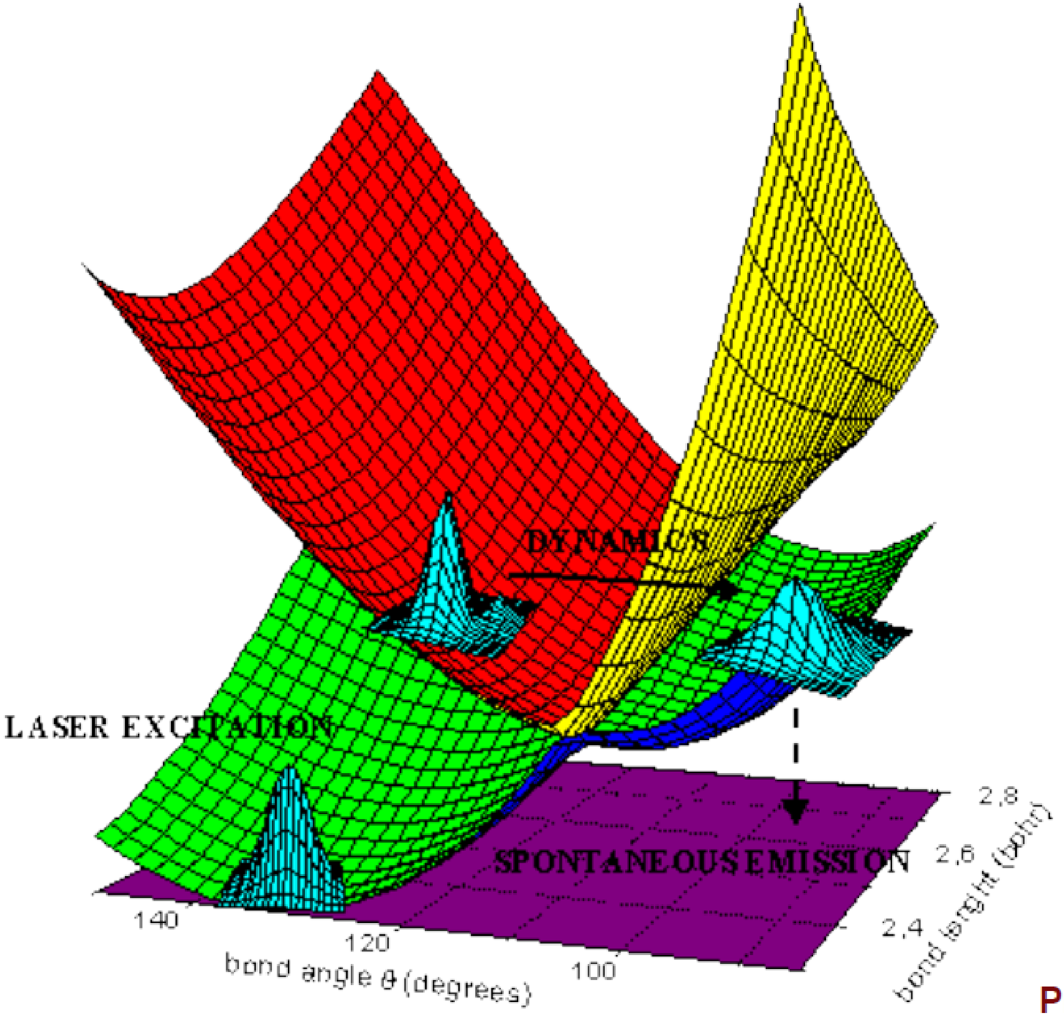
Can two states have the same energy E*?*

Requires $H_{11} = H_{22}$ and $H_{12} = 0$

This restricts two degrees of freedom and is thus not possible in a diatomic (avoided crossing rule) but it is possible for larger molecules (conical intersection) and indeed multiple *electronic states can be degenerate provided sufficient numbers of degrees of freedom are available to satisfy the necessary constraints.*

(CI too)

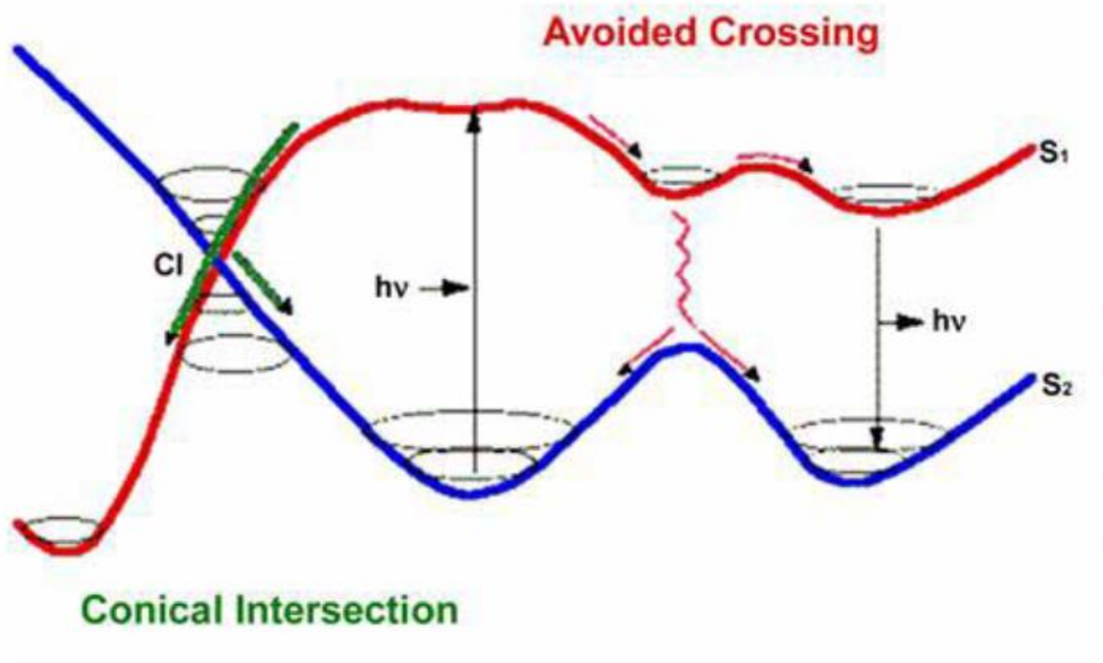
Conical Intersection Example (NO_2)



Note that 3 atoms leaves one final degree of freedom, so the CI is not a point, but a "seam" (that has a minimum)

Professor Carlo Petrongolo

Conical Intersection Example 1D Projection



CIs permit radiationless transitions from one state to another. Kasha's rule says that such internal conversions among excited states will be very fast until one reaches S_1 (the first state above the ground state S_0)

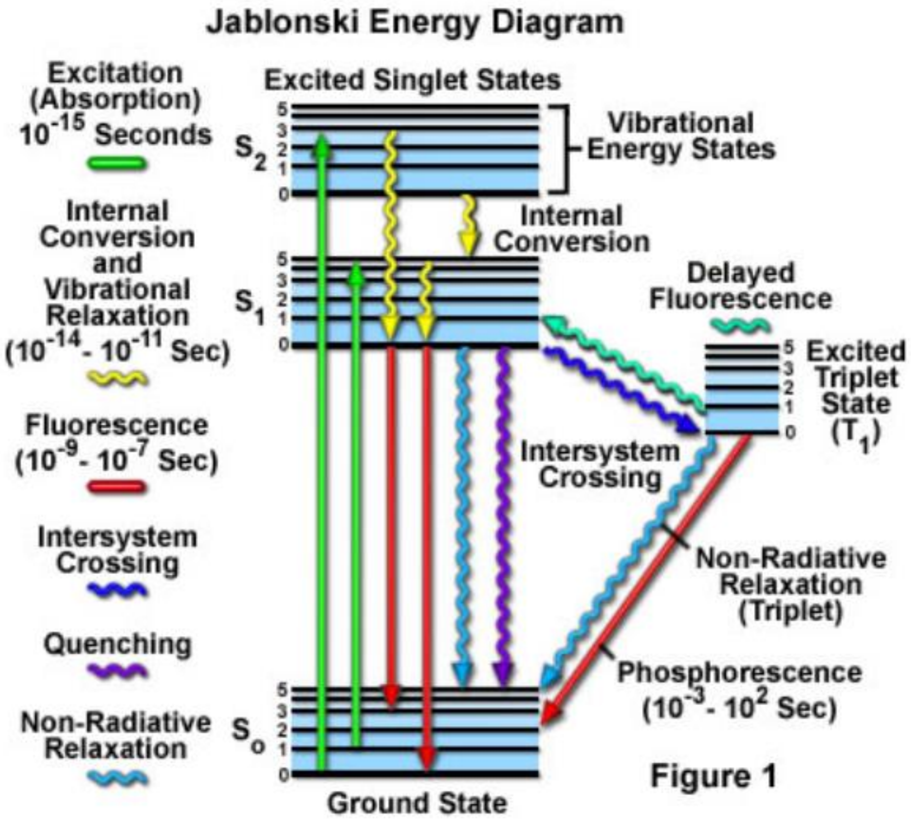
What If Two States Have Different Spin Multiplicity?

- In non-relativistic quantum mechanics, transitions between two states of different spin multiplicity are strictly forbidden (although it is mildly paradoxical to refer to spin at all if one is imagining non-relativistic QM)
- However, a relativistic Hamiltonian includes operators that affect spin, including the spin-orbit operator, the spin-spin dipole operator (coupling two electrons) and the hyperfine operator (coupling electronic and nuclear spins)
- Spin-orbit coupling increases with the 4th power of the atomic number, so with heavier nuclei, this process can be very efficient

$$H_{\mathrm{SO}} \approx \frac{1}{c^2} \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{Z_k^4}{\left|r_{ik}\right|^3} l_j \bullet s_j$$

Mainly responsible for all spin forbidden processes. Also 2-e terms

Nondynamical Photophysical Processes for a Single Geometry

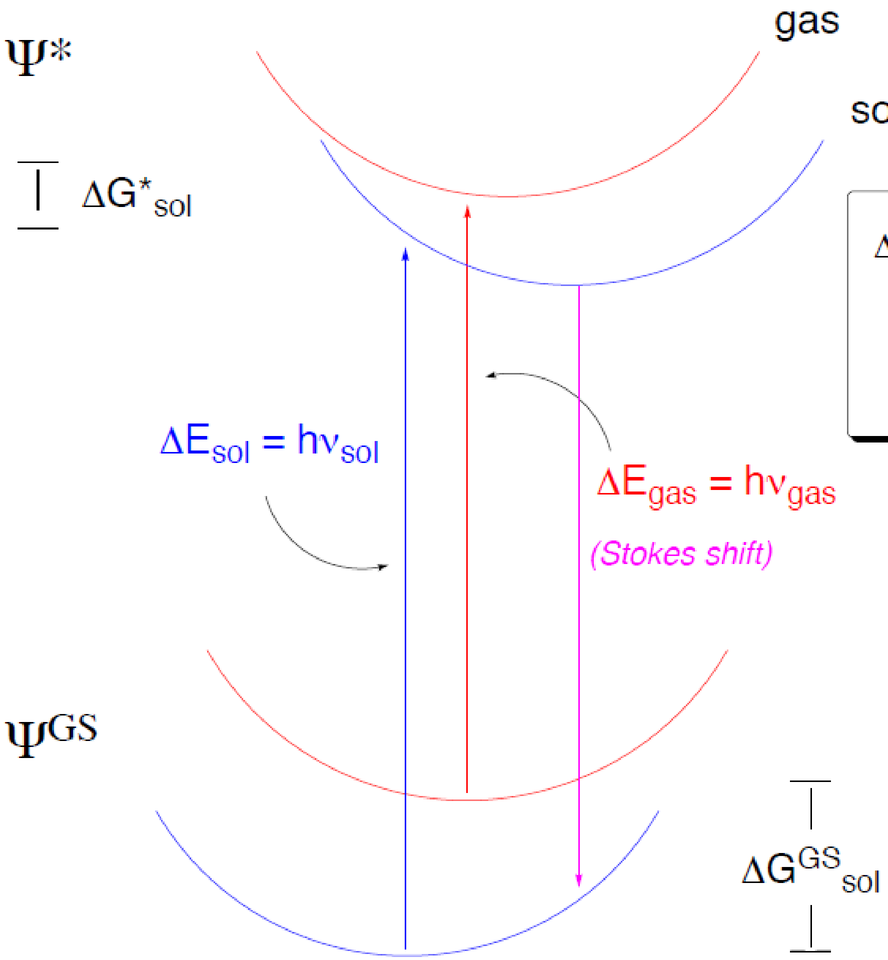


Dynamics adds substantial complication by changing relative state energies. Solvation compounds the difficulty by changing state energies in a time-dependent fashion as non-equilibrium solvation decays to equilibrium solvation

Collisions usually involve excited states and many states of ions

Solvatochromism Redux

Equilibrium vs. Nonequilibrium Solvation



$$\Delta E_{sol} = \Delta E_{gas} + \underbrace{\Delta G^{*}_{sol} - \Delta G^{GS}_{sol}}_{\textit{solvatochromic effect}}$$

Solvation energy can be computed using many different models!

- Excited states calculations usually require larger basis set and better treatment of electron correlations to achieve the same level of accuracy as the ground state.
- Electronic structure of ions can be calculated similarly

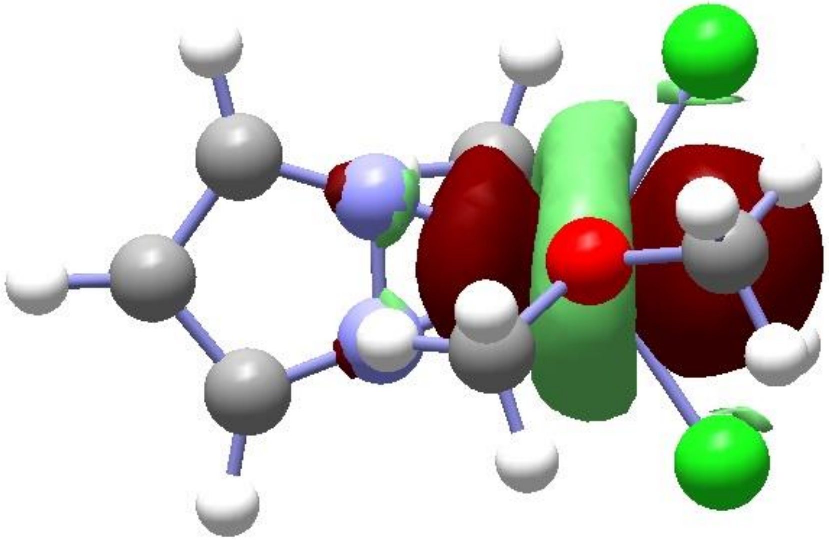
One-electron properties and MO

- MO is not an physical observable by itself
- MO can be used to explain chemical and physical properties.
- MO is also useful for qualitative interpretation

Molecular Orbital Plots

$$\phi_{\mathrm{i}}(\vec{r}) = \sum_{\mu} c_{\mu \mathrm{i}} \chi_{\mu}(\vec{r})$$

- plot a surface where $|\phi_{\mathrm{i}}(\mathrm{r})|^2 = \mathrm{c}$
- $\phi_{\mathrm{i}}(\mathrm{r})$ can have positive and negative values
- shade in different colors
- only the change in sign matters, not the absolute sign



Population Analysis

- divide up the total electron density into contributions from the individual atoms or basis functions
- each orbital is normalized

$$\int \phi_i^* \phi_i \, d\tau = 1$$

- in a closed shell molecule, each occupied orbital contains 2 electrons (N_e is the total number of electrons)

$$\sum_i^{occ} 2 \int \phi_i^* \phi_i \, d\tau = N_e$$

Population Analysis

- each orbital is a linear combination of basis functions

  $$\phi_i = \sum_{\mu} c_{\mu i} \chi_{\mu}$$

- plug into the expression for the total number of electrons and rearrange terms

  $$\sum_{i}^{occ} 2 \int \phi_i^* \phi_i \, d\tau = N_e$$

  $$\sum_{i}^{occ} 2 \int \{\sum_{\mu} c_{\mu i}^* \chi_{\mu}\}\{\sum_{\nu} c_{\nu i} \chi_{\nu}\} d\tau = N_e$$

  $$\sum_{\mu\nu} \{\sum_{i}^{occ} 2 c_{\mu i}^* c_{\nu i}\} \; \{\int \chi_{\mu} \chi_{\nu} \, d\tau\} = \sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu} = N_e$$

Population Analysis

$$\sum_{i}^{occ} 2c_{\mu i}^{*} c_{\nu i} = P_{\mu\nu} \quad \textit{density matrix,} \quad S_{\mu\nu} \ \textit{overlap matrix}$$

- partition $\sum_{\mu\nu} P_{\mu\nu} S_{\mu\nu} = N_e$ into contributions from different atoms and basis functions

$$M_{\mu\nu} = P_{\mu\nu} S_{\mu\nu} \ \textit{Mulliken population analysis matrix}$$

$$M_{AB} = \sum_{\mu\in A} \sum_{\nu\in B} P_{\mu\nu} S_{\mu\nu} \quad \textit{condensed to atoms}$$

$$q_A = Z_A - \sum_{B} M_{AB} \quad \textit{atomic charge}$$

Dipole Moment

- for Hartree-Fock wavefunctions, the dipole is the expectation value of the classical expression for the dipole
- can be written in terms of the density matrix and a set of dipole integrals over the basis functions

$$\vec{\mu} = \int \psi^* \left(\sum_i -e\vec{r}_i\right)\psi \, d\tau + \sum_A eZ_A \vec{R}_A$$

$$= \sum_i^{occ} 2\int \phi_i^* (-e\vec{r})\phi_i \, d\tau + \sum_A eZ_A \vec{R}_A$$

$$= \sum_{\mu\nu} P_{\mu\nu} \int \chi_\mu (-e\vec{r})\chi_\nu \, d\tau + \sum_A eZ_A \vec{R}_A$$

Electron Density

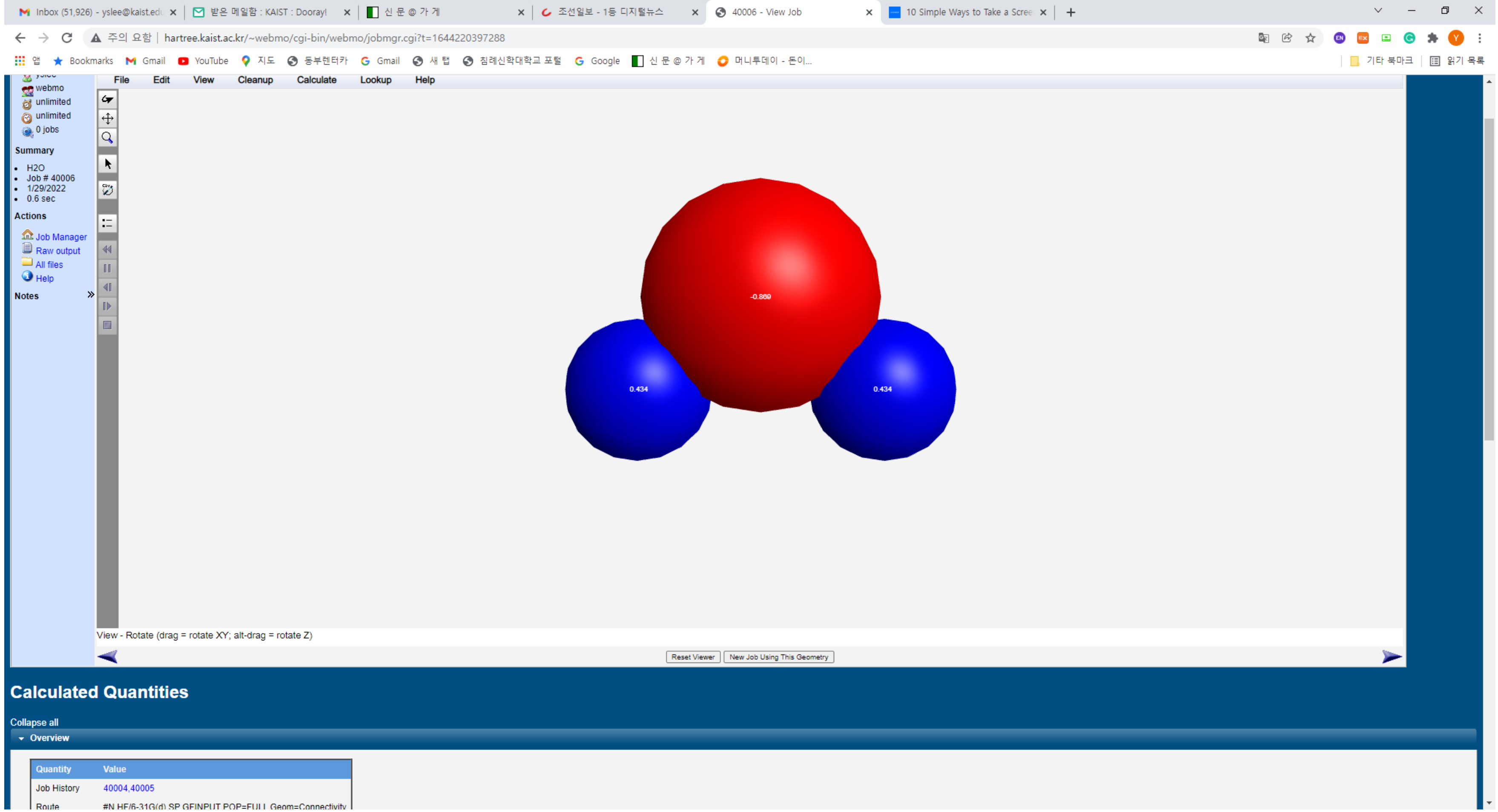
$$\rho(\vec{r}) = \sum_{\mu\nu} P_{\mu\nu} \chi_{\mu}(\vec{r}) \chi_{\nu}(\vec{r})$$

Electrostatic Potential

- energy of a unit test charge placed at r_C

$$ESP(\vec{r}_C) = \int \psi^{*} (-e/\vec{r}_C) \psi \, d\tau + \sum_{A} eZ_A / \vec{R}_{AC}$$

$$= \sum_{\mu\nu} P_{\mu\nu} \int \chi_{\mu} (-e/\vec{r}_C) \chi_{\nu} \, d\tau + \sum_{A} eZ_A / \vec{R}_{AC}$$



Summary

- H2O
- Job # 40006
- 1/29/2022
- 0.6 sec

Actions

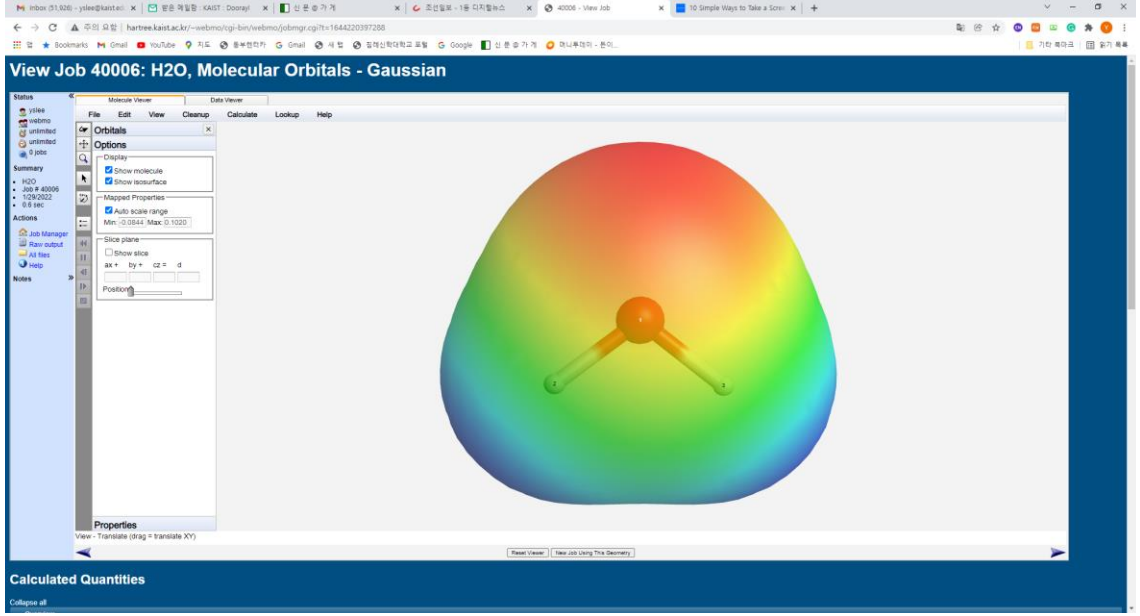
- Job Manager
- Raw output
- All files
- Help

Notes

View - Rotate (drag = rotate XY; alt-drag = rotate Z)

Calculated Quantities

Quantity	Value
Job History	40004,40005
Route	#N HF/6-31G(d) SP GFINPUT POP=FULL Geom=Connectivity



View Job 40006: H2O, Molecular Orbitals - Gaussian

Summary
- H2O
- Job # 40006
- 1/29/2022
- 0.6 sec

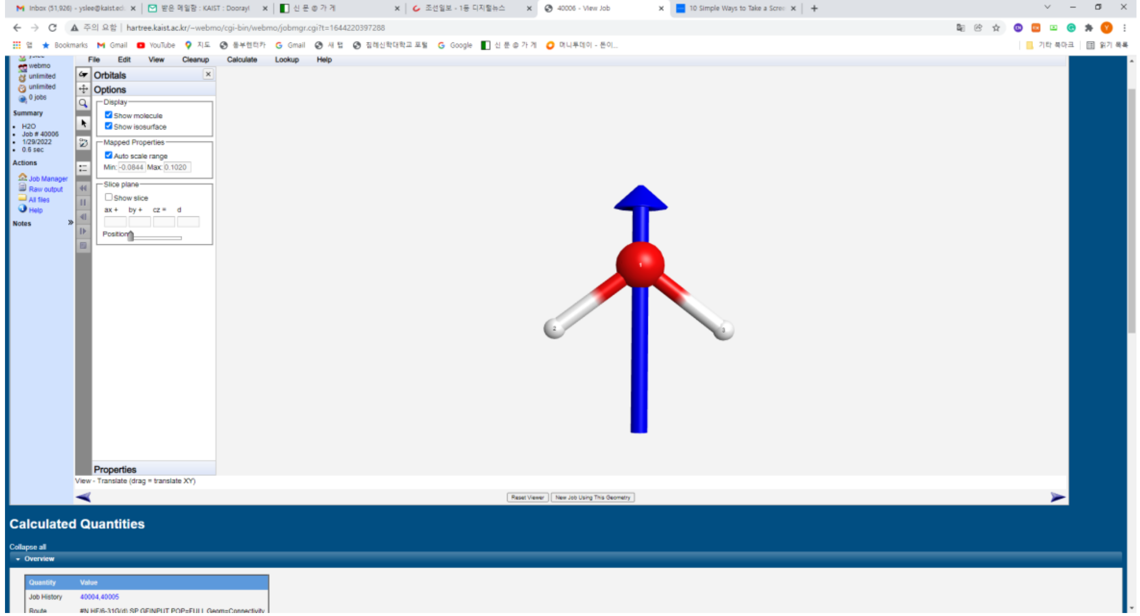
Display
- ☑ Show molecule
- ☑ Show isosurface

Mapped Properties
- ☑ Auto scale range
- Min: -0.0844 Max: 0.1020

Slice plane
- ☐ Show slice

View - Translate (drag = translate XY)

Calculated Quantities



Display
- ☑ Show molecule
- ☑ Show isosurface

Mapped Properties
- ☑ Auto scale range
- Min: -0.0844 Max: 0.1020

Slice plane
- ☐ Show slice

View - Translate (drag = translate XY)

Calculated Quantities

Overview

Quantity	Value
Job History	40004,40005
Route	#N HF/6-31G(d) SP GFINPUT POP=FULL Geom=Connectivity

Partial Atomic Charges (in molecules)

- Class 1 : from chemical intuition such as electronegativity
- Class 2: Direct partitioning of wave function
  - Mulliken
  - Lowdin
  - Natural bond analysis
  - & more
- Class 3: through analysis of some physical observables
  - Fit to density or electrostatic potential
- Class 4: semiempirical mapping of a precursor charge to match experimentally derived quantities (Class 2 or 3 charges with corrections)

ground state properties

bulk properties

- density
- viscosity, hardness
- dielectric constant
- melting point

⋮

molecular properties

- dipole moment
- polarizability
- NMR chemical shift
- vibrational frequency

⋮

When the corresponding operator O and the wavefunction are known, the property can be calculated as the expectation value !

a more general approach

property = response of a molecule to a perturbation (λ)

change in energy

- change in geometry (R)
- external electric field (F)
- external magnetic field (M)
- nuclear magnetic field (I)

Taylor expansion: $$E(\lambda) = E(0) + \underbrace{\frac{\partial E}{\partial \lambda}}_{\text{first order}}\lambda + \frac{1}{2}\underbrace{\frac{\partial^2 E}{\partial \lambda^2}}_{\text{second order}}\lambda^2 + \frac{1}{6}\underbrace{\frac{\partial^3 E}{\partial \lambda^3}}_{\text{third order}}\lambda^3 + \dots$$

property

λ is usually *directed,* i.e. represented by a *vector* (field)

$$\Rightarrow \quad \frac{\partial E}{\partial \lambda} = \text{vector} \qquad \frac{\partial^2 E}{\partial \lambda^2} = \text{matrix} \qquad \frac{\partial^3 E}{\partial \lambda^3} = \text{tensor}$$

properties that can be formulated (and calculated) as derivatives of the energy

nth derivative with regard to

change in geometry (R), external electric field (F)
external magnetic field (M, nuclear magnetic field (I)

n_R	n_F	n_B	n_I	Property
1	0	0	0	Energy gradient $\boldsymbol{g}$
2	0	0	0	Harmonic vibrational frequencies ω_i
3	0	0	0	(cubic) anharmonic corrections to vibrational frequecies $\omega_i x_i$
0	1	0	0	Electric dipole moment μ
0	2	0	0	Electric polarizability α
0	3	0	0	(first electric) hyperpolarizability β
0	0	1	0	Magetic (dipole) moment μ
0	0	2	0	magnetic susceptibility χ
0	0	0	1	ESR hyperfine coupling constant $\boldsymbol{a}_i$
0	0	0	2	Spin-spin coupling $\boldsymbol{J}_{ij}$ of different nuclei
1	1	0	0	Intensities of fundamental IR transitions
2	1	0	0	Intensities of overtones and combination bands in IR spectra
1	2	0	0	Intensities of fundamental Raman transitions
2	2	0	0	Intensities of overtones and combination bands in Raman spectra
0	1	1	0	Circular dichroism (CD)
0	2	1	0	Magnetic circular dichroism (MCD)
0	0	1	1	Nuclear magnetic shielding (→ chemical shift in NMR)

mixed derivatives
.
.
.
.
.

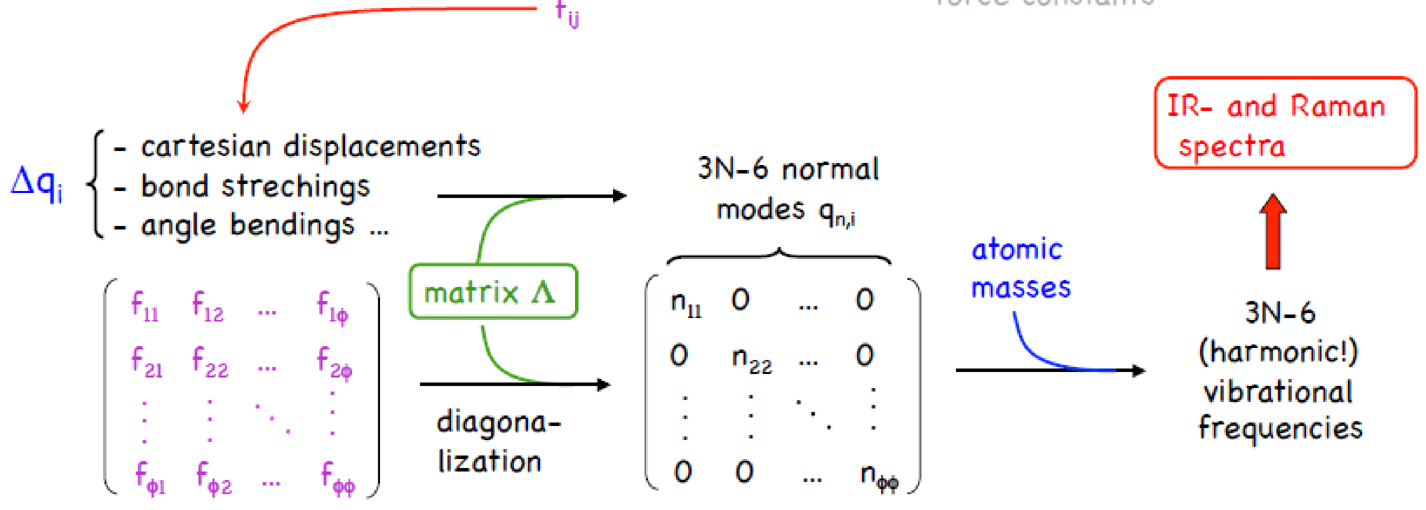
1. perturbation = deviation from *equilibrium geometry* (Δq)

(molecule with ϕ = 3N-6 internal degrees of freedom)

$$E(\Delta q_i) = E(0) + \underbrace{\frac{\partial E}{\partial \Delta q_i}}_{\substack{\text{gradients} \\ g_i}} \Delta q_i + \underbrace{\frac{\partial^2 E}{\partial \Delta q_i \partial \Delta q_j}}_{\substack{\text{harmonic} \\ \text{force constants} \\ f_{ij}}} \Delta q_i \cdot \Delta q_j + \underbrace{\frac{\partial^3 E}{\partial \text{“}\Delta q_i^3\text{”}}}_{\text{cubic}} \text{“}\Delta q_i^3\text{”} + \underbrace{\frac{\partial^4 E}{\partial \text{“}\Delta q_i^4\text{”}}}_{\text{quartic}} \text{“}\Delta q_i^4\text{”} + \ldots$$

...... force constants

= 0 at equilibrium ← gradients g_i



Δq_i
- cartesian displacements
- bond strechings
- angle bendings ...

$$\begin{pmatrix} f_{11} & f_{12} & \cdots & f_{1\phi} \\ f_{21} & f_{22} & \cdots & f_{2\phi} \\ \vdots & \vdots & \ddots & \vdots \\ f_{\phi 1} & f_{\phi 2} & \cdots & f_{\phi\phi} \end{pmatrix} \xrightarrow[\text{diagona-lization}]{\text{matrix } \Lambda} \underbrace{\begin{pmatrix} n_{11} & 0 & \cdots & 0 \\ 0 & n_{22} & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & n_{\phi\phi} \end{pmatrix}}_{}$$

3N-6 normal modes $q_{n,i}$

atomic masses → 3N-6 (harmonic!) vibrational frequencies → **IR- and Raman spectra**

Intensities: calculated from mixed derivatives (see later)

prediction of vibrational spectra: some rules

1. calculation of vibrational spectra makes only physical sense *at potential energy minima*!
   always make sure that your structure is fully optimized, and that all frequecies are positive!

2. agreement between *individual* frequencies in calculated and measured vibrational spectra is *absolutely meaningless*.

   only a general agreement of the *entire spectral pattern* serves as an assignment tool. *All* important predicted bands should appear in the measured spectrum and vice versa!

3. big molecules (with no symmetry) have *very many* vibrational transitions

   the bigger your molecule, the more likely you will discern a general agreement between a calculated and a measured spectrum (if you kink your head and squint your eyes)

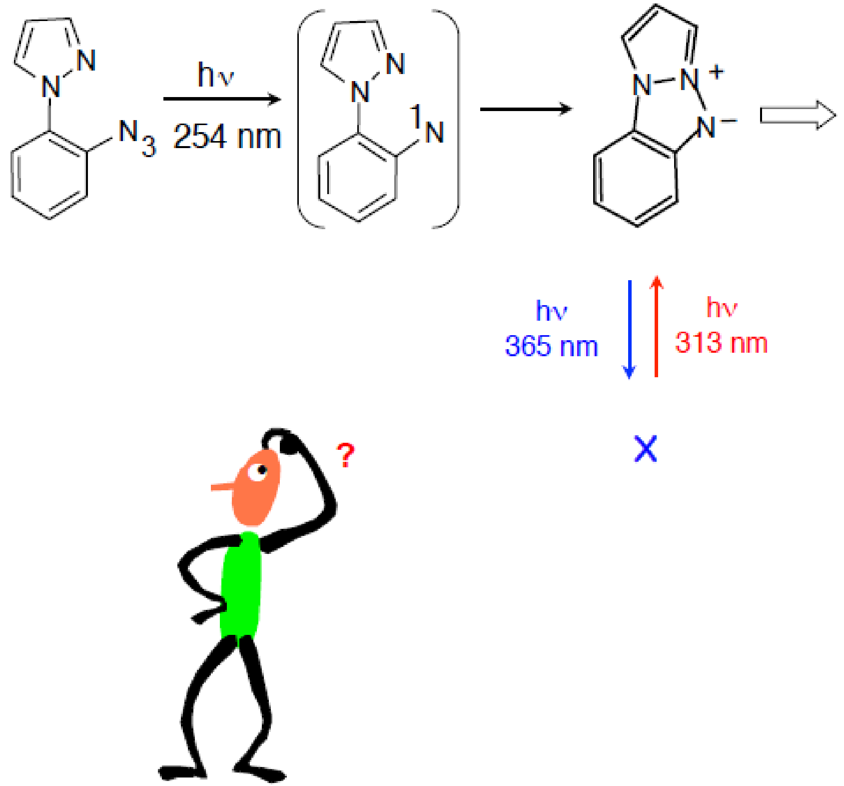
4. never use calculations as a substitute for chemical common sense.

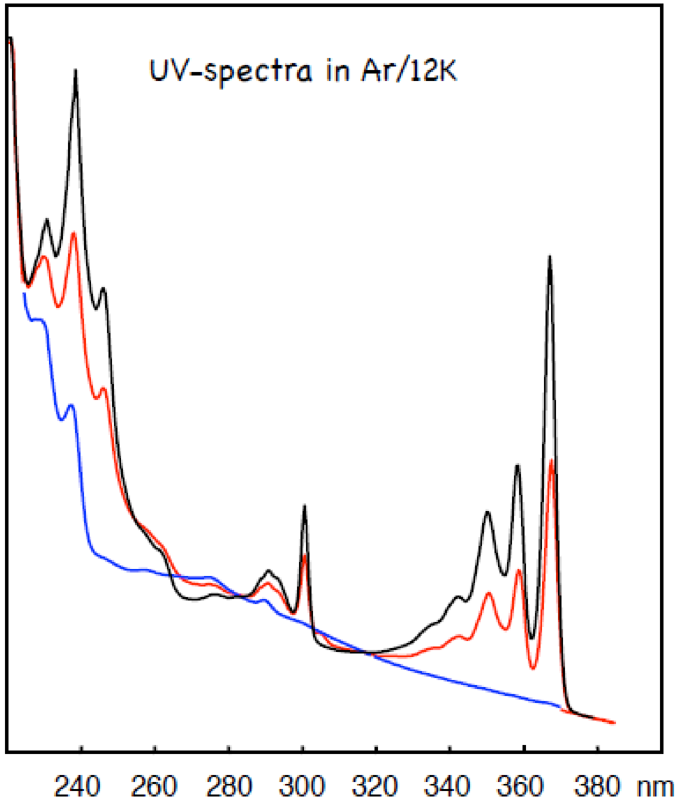
   what you learned in analytical chemistry about *group frequencies* may be more useful than the results of quantum chemical calculations

5. never forget that what you calculate are always *fundamental harmonic* frequencies.
   - experimental spectra may contain *overtones, combination bands,* or *Fermi resonances*
   - deviations between theory and experiment may be due to anharmonicities

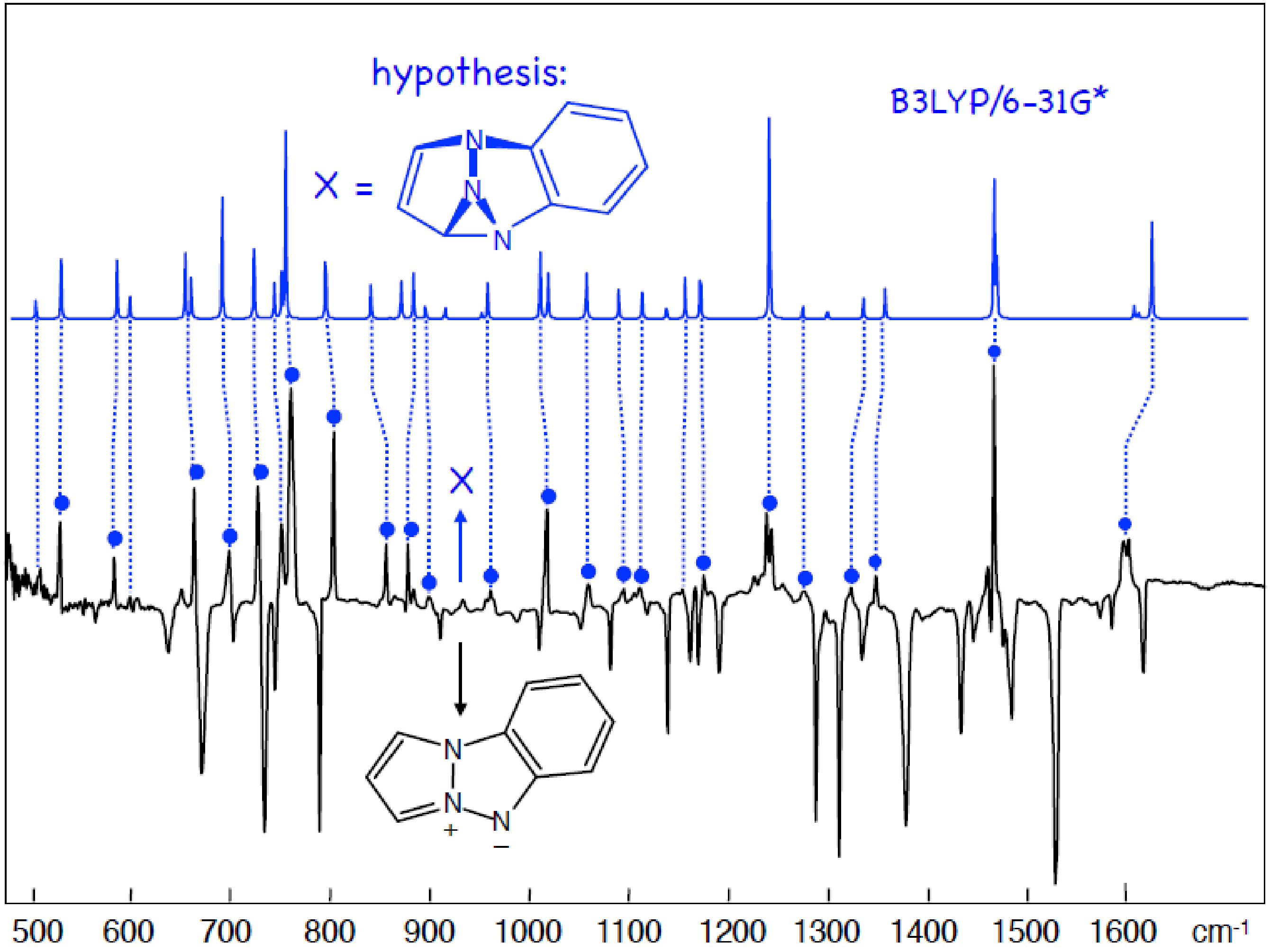
an example

O-Pyrazolylphenylnitrene

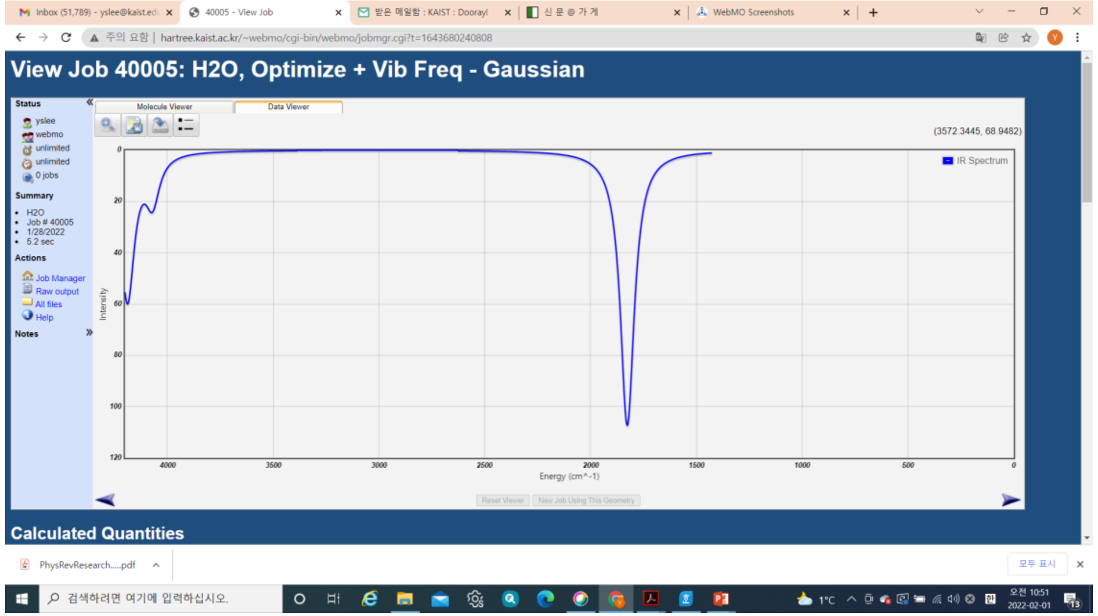




"pattern matching"



Simulated IR and Raman spectra using calculated vibrational frequencies



View Job 40005: H2O, Optimize + Vib Freq - Gaussian

Status
- yslee
- webmo
- unlimited
- unlimited
- 0 jobs

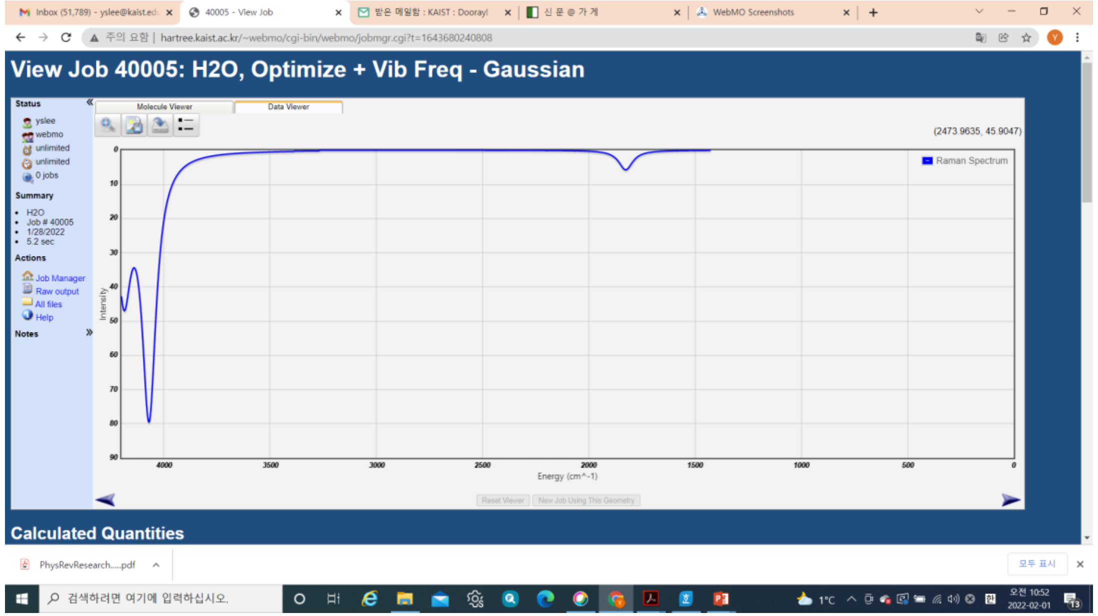
Summary
- H2O
- Job # 40005
- 1/28/2022
- 5.2 sec

Actions
- Job Manager
- Raw output
- All files
- Help

Notes

(3572.3445, 68.9482)

Calculated Quantities



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- unlimited
- unlimited
- 0 jobs

Summary
- H2O
- Job # 40005
- 1/28/2022
- 5.2 sec

Actions
- Job Manager
- Raw output
- All files
- Help

Notes

(2473.9635, 45.9047)

Calculated Quantities

what method to use to calculate IR-spectra ?

see the large study by Scott and Radom, *J. Phys. Chem.* 100, 16502 (1996)
(122 molecules, 1066 fundamentals).

HF/6-31G*	large (100 cm^{-1}) systematic errors, many outliers
MP2/6-31G*	smaller (65 cm^{-1}) unsystematic errors, fewer outliers
BLYP/6-31G*	quite small (40 cm^{-1}) unsystematic errors, very few outliers
B3LYP/6-31G*	smaller (35 cm^{-1}) partially systematic errors, very few outliers

↓ or other hybrid functionals

↘ no bigger basis set needed!

↓ scale by a factor (ca 0.96)

X-H stretching frequencies are usually off by more than the others, due to strong anharmonicity. They are often not useful for identifying molecules, also because of the presence of overtones and Fermi resonances in the region 2800-3300 cm^{-1}.

if your molecule is too big to run a frequency calculation with a hybrid DFT functional and a DZP basis set, then it is probably too big to allow for a reliable comparison between ~~calculation~~ and experiment.

2. perturbation = external electric field (F)

F = perturbation of the *potential energy term* V in the Hamiltonian
(quite simple to implement, as V is a simple multiplier)

$$E(F) = E(0) + \underbrace{\frac{\partial E}{\partial F}}_{\substack{\mu_0 \\ \text{dipole} \\ \text{moment}}} F + \frac{1}{2}\underbrace{\frac{\partial^2 E}{\partial F^2}}_{\substack{\alpha \\ \text{polariz-} \\ \text{ability}}} F^2 + \frac{1}{6}\underbrace{\frac{\partial^3 E}{\partial F^3}}_{\substack{\beta \\ \text{(first)} \\ \text{hyperpol-} \\ \text{arizability}}} F^3 + \underbrace{\;\ldots\;}_{\substack{\text{higher hyper-} \\ \text{polarizabilities}}}$$

a) Dipole moments, μ_0/Debye

Molecule	exp	HF/ 6-31G*	HF/ POL	MP2/ 6-31G*	MP2/ POL	B3LYP cc-pVTZ	B3LYP POL
CO	0.11	-0.26	-0.17	0.33	0.31	0.13	0.10
H_2O	1.85	2.20	1.98	2.16	1.85	1.92	1.86
H_2S	0.97	1.41	1.11	1.49	1.03	1.19	1.01
NH_3	1.47	1.92	1.62	1.92	1.52	1.59	1.52
HF	1.83	1.98	1.92	1.98	1.80	1.83	1.80

POL: Sadlei's pVTZ basis set, optimized for electrical properties

↱ $\langle\alpha\rangle = 1/3\cdot(\alpha_{xx}+\alpha_{yy}+\alpha_{zz})$

b) mean (static) polarizabilites, $\langle\alpha\rangle$/a.u. (1 a.u.= 0.1482 Å³)

Molecule	exp	HF/ 6-31G*	HF/ POL	MP2/ 6-31G*	MP2/ POL	B3LYP cc-pVTZ	B3LYP POL
CO	13.08	9.25	12.23	9.54	13.09	11.11	13.18
H_2O	9.64	4.87	8.51	4.93	9.80	7.07	9.96
H_2S	24.71	14.45	23.77	14.20	24.70	18.54	25.24
NH_3	14.56	7.93	12.94	7.93	14.42	10.97	14.73
HF	5.60	2.68	4.88	2.73	5.67	1.95 (!)	5.83

Here, the POL basis set really helps!

↱ $\langle\beta\rangle = 3/5\cdot(\beta_{xxz}+\beta_{yyz}+\beta_{zzz})$

c) mean (static) first hyperpolarizabilites, $\langle\beta\rangle$/a.u.

⇩

difficult to measure, comparisons can only be made to very good calculations

hybrid DFT methods do reasonably well, but *diffuse basis functions* are needed

3. perturbation = external magnetic field (B)

$$E(B) = E(0) + \underbrace{\frac{\partial E}{\partial B}}_{m_0} B + \frac{1}{2}\underbrace{\frac{\partial^2 E}{\partial B^2}}_{\xi/\mu_0} B^2 + \ldots$$

m_0
(permanent)
magnetic
dipole moment

=0 for closed-shell compounds

$\xi/\mu_0 \longrightarrow$ vacuum permeability
(relative)
magnetic
permeability

related to the (macroscopic)
magnetic susceptibility

B interacts with the *magnetic moments* of the electrons caused by their *movement*, i.e. it is a perturbation to the *kinetic energy* or *momentum* term in the Hamiltonian. This perturbation is determined by the magnetic field's *vector potential* A(r).

Vector potentials are always defined relative to an *origin*, the "gauge" r_G.
➡ the results of calculations are origin or gauge-depenent!

Different solutions have been proposed to this problem. The two most popular are:

a) each basis function includes its own origin
(Gauge Including Atomic Orbitals, GIAO, London 1937 ⬅ imlemented in the Gaussian program

b) MOs are localized such that they have their own origins
(Individual Gauge for Localized Orbitals, IGLO, Kutzlnigg 1982

3. perturbation = external magnetic field (B)

- rarely does one do calculations of magnetic susceptibilities.
- In practice, chemists use external magnetic fields as a means to let *other perturbations* manifest themselves (nuclear magnetic shielding, hyperfine coupling, MCD ...). such as:

4. perturbation = nuclear magnetic moments (I)

- nuclei j with nonzero spin (^{1}H, ^{13}C, ^{15}N ...) have magnetic moments I_j.
- These give rise to magnetic fields inside molecules.
- By analogy to the first three cases we write:

$$E(I_i, I_j \ldots) = E(0) + \underbrace{\frac{\partial E}{\partial I_i}}_{a_i} I_i + \underbrace{\frac{\partial^2 E}{\partial I_i \partial I_j}}_{h\cdot J_{ij}} I_i \cdot I_j + \ldots\ldots$$

ESR hyperfine coupling constant $\Leftarrow a_i$

$h\cdot J_{ij} \Rightarrow$ nuclear spin-spin coupling constant

5. two simultaneous perturbations

In the presence of two perturbation acting simultaneously, the energy is expanded in both perturbation, which leads to *mixed derivatives*, many of which are also related to molecular properties.

2-D spectroscopy?

a) IR intensities: change in dipole moment μ for deformation along normal coordinate $q_{n,ii}$

in the "double harmonic approximation" (termination at first order):

$$\text{IR intensity } (q_{n,i}) \propto \left(\frac{\partial \mu}{\partial q_{n,i}}\right)^2 \underset{\uparrow}{\propto} \left(\frac{\partial^2 E}{\partial q_{n,i} \partial F}\right)^2$$

$$\text{dipole moment } \mu = \frac{\partial E}{\partial F}$$

b) Raman intensities: change in polarizability α for deformation along normal coordinate $q_{n,ii}$

in the "double harmonic approximation" (termination at first order):

$$\text{Raman intensity } (q_{n,i}) \propto \left(\frac{\partial \alpha}{\partial q_{n,i}}\right)^2 \underset{\uparrow}{\propto} \left(\frac{\partial^3 E}{\partial q_{n,i} \partial F^2}\right)^2$$

$$\text{polarizability } \alpha = \frac{\partial^2 E}{\partial F^2}$$

Note: IR- and Raman-intensities are proportional to derivatives of *electrical properties*. Remember that, to get those right, one needs special basis sets (e.g. Sadlej POL)

c) nuclear magnetic "shielding" (by the local magentic fields that arise from the circular movements of electrons induced by the external magnetic field B)

nuclear magnetic shielding constant $\sigma(B) \propto \left(\frac{\partial^2 E}{\partial B \partial I_i}\right)^2$

$\Downarrow$

translates into NMR chemical shift

$\delta = 10^6 \times (\sigma - \sigma_0)(B)$

Finally, perturbations can also be *time dependent*.

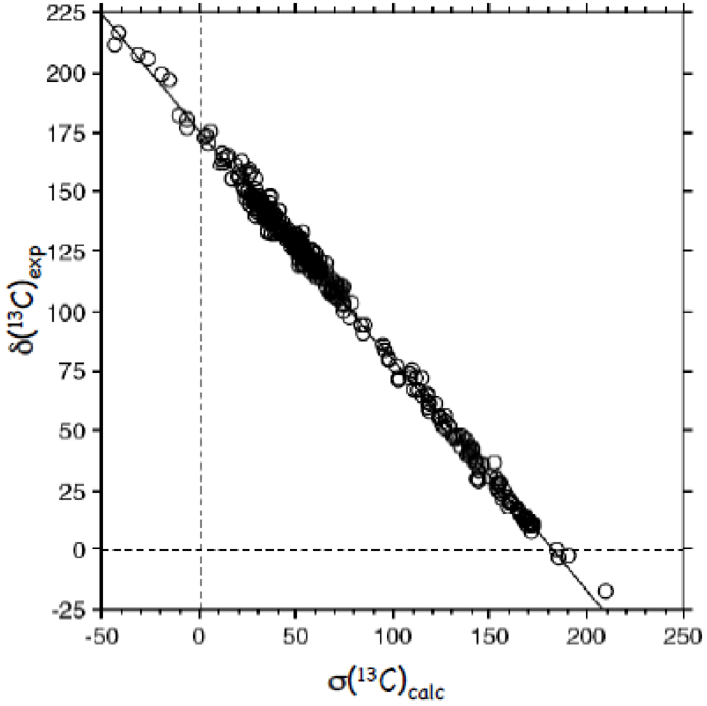
In particular, electromagnetic radiation represents electric fields $F(t)$ and magnetic fields $B(t)$, oscillating with a frequency ω, which perturb the movements and the distribution of electrons in a molecule. See last lecture by Prof. Cramer

In particular electronic absorption spectra can be regarded (and calculated) as espressions of the *time-dependent polarizability* of a ground-state distribution of electrons (see last module by Prof. Cramer).

But now, back to applications!

Akorta et al. (Madrid)

461 ^{13}C chemical shifts calculated by GIAO/B3LYP/6-311++G(d,p)

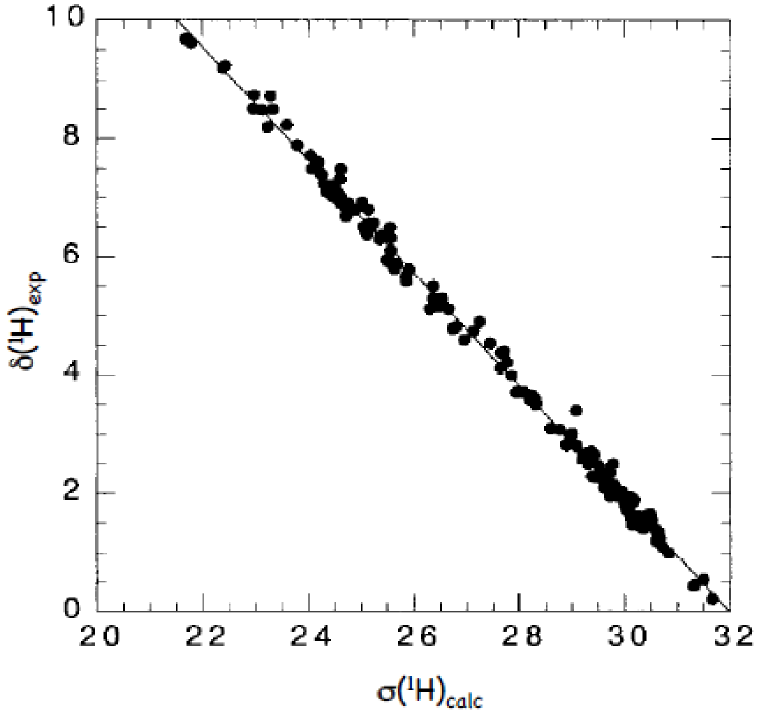


$\delta(^{13}C)_{exp} = 175.7 - 0.963\times\sigma(^{13}C)_{calc}$

r^2=0.996, rms error: 2.9 ppm

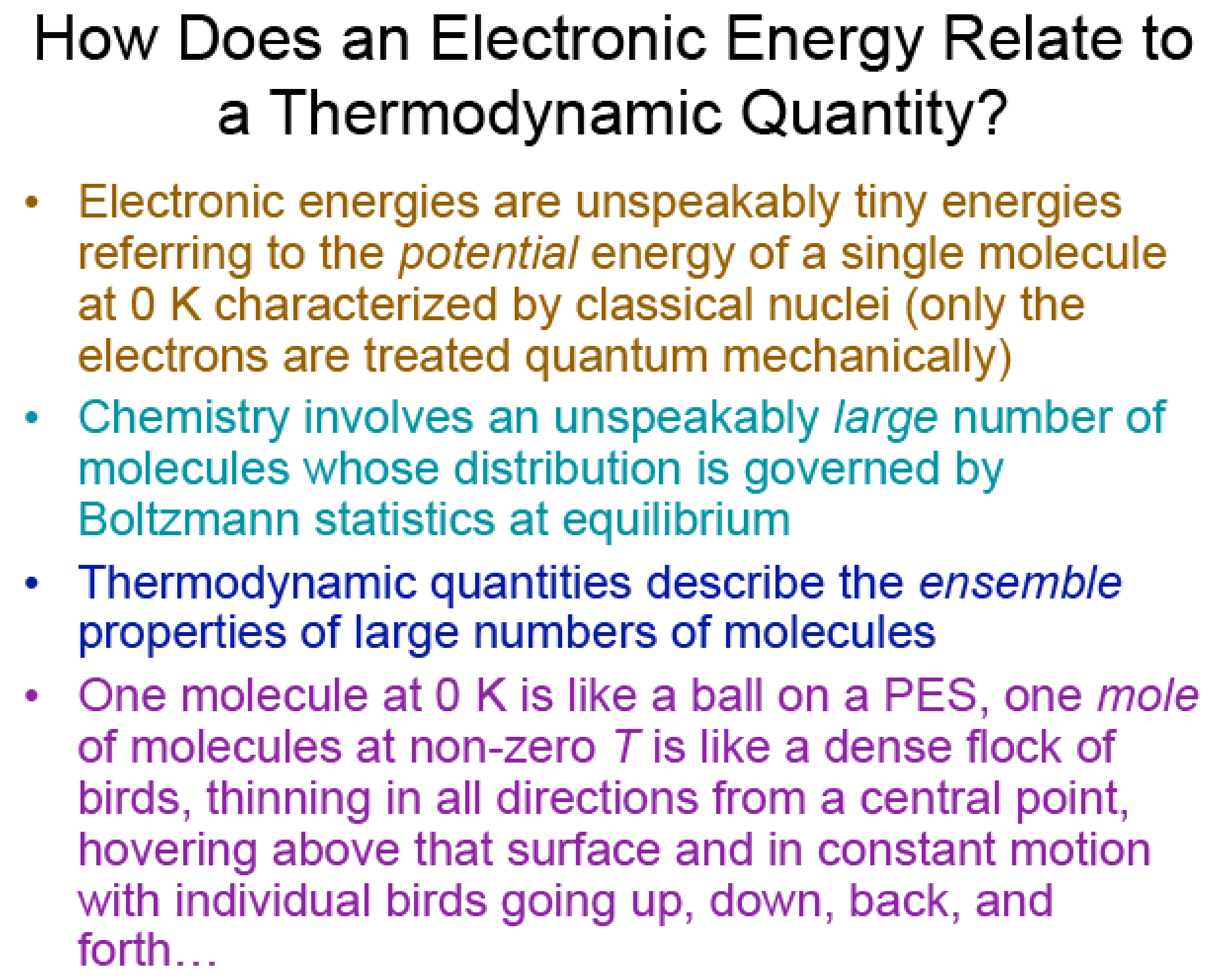
Rablen et al. (Swarthmore Coll.)

^1H chemical shifts of 80 organic compounds calculated by GIAO/B3LYP/6-311++G(d,p)



$\delta(^1H)_{exp} = 30.6 - 0.957\times\sigma(^1H)_{calc}$

r^2=0.996, rms error: 0.15 ppm



How Does an Electronic Energy Relate to a Thermodynamic Quantity?

- Electronic energies are unspeakably tiny energies referring to the *potential* energy of a single molecule at 0 K characterized by classical nuclei (only the electrons are treated quantum mechanically)
- Chemistry involves an unspeakably *large* number of molecules whose distribution is governed by Boltzmann statistics at equilibrium
- Thermodynamic quantities describe the *ensemble* properties of large numbers of molecules
- One molecule at 0 K is like a ball on a PES, one *mole* of molecules at non-zero *T* is like a dense flock of birds, thinning in all directions from a central point, hovering above that surface and in constant motion with individual birds going up, down, back, and forth…

Fundamental Equations of Thermodynamics

Canonical ensemble

The partition function

$$Q(N,V,T) = \sum_i e^{-E_i(N,V)/k_B T}$$

Internal energy

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

Enthalpy

$$H = U + PV$$

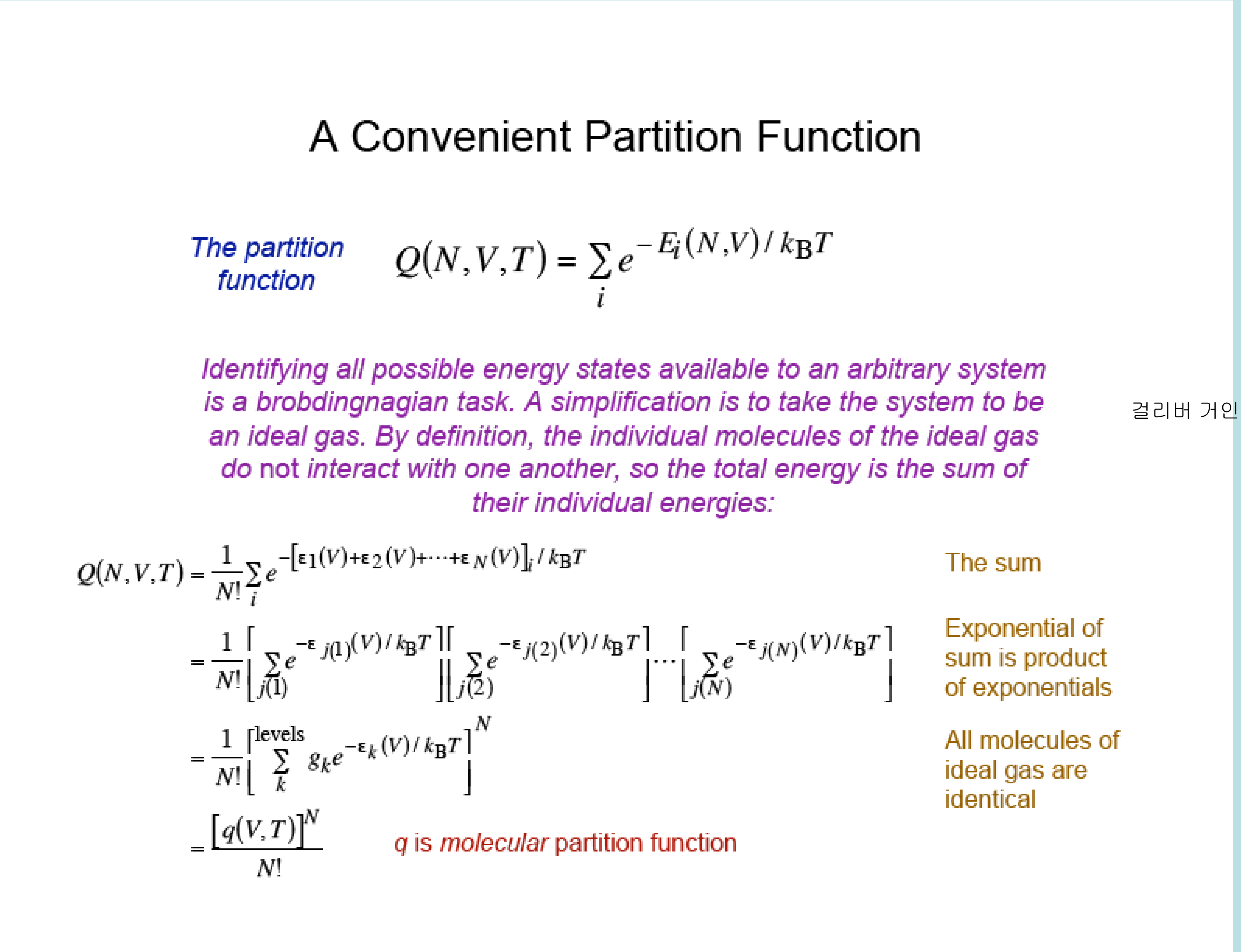
Entropy

$$S = k_B \ln Q + k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

Gibbs Free Energy
(Free Enthalpy)

$$G = H - TS$$

Note how in thermodynamics the partition function has essentially the same status as the wave function has in quantum mechanics



A Convenient Partition Function

The partition function

$$Q(N,V,T) = \sum_i e^{-E_i(N,V)/k_\mathrm{B}T}$$

Identifying all possible energy states available to an arbitrary system is a brobdingnagian task. A simplification is to take the system to be an ideal gas. By definition, the individual molecules of the ideal gas do not interact with one another, so the total energy is the sum of their individual energies:

걸리버 거인국의

$$Q(N,V,T) = \frac{1}{N!}\sum_i e^{-[\varepsilon_1(V)+\varepsilon_2(V)+\cdots+\varepsilon_N(V)]_i/k_\mathrm{B}T}$$

The sum

$$= \frac{1}{N!}\left[\sum_{j(1)} e^{-\varepsilon_{j(1)}(V)/k_\mathrm{B}T}\right]\left[\sum_{j(2)} e^{-\varepsilon_{j(2)}(V)/k_\mathrm{B}T}\right]\cdots\left[\sum_{j(N)} e^{-\varepsilon_{j(N)}(V)/k_\mathrm{B}T}\right]$$

Exponential of sum is product of exponentials

$$= \frac{1}{N!}\left[\sum_k^{\text{levels}} g_k e^{-\varepsilon_k(V)/k_\mathrm{B}T}\right]^N$$

All molecules of ideal gas are identical

$$= \frac{[q(V,T)]^N}{N!}$$

q is *molecular* partition function

What Contributes to the Total Energy of a Molecule?

Electronic energy: (from Schrödinger or Kohn-Sham eqs)

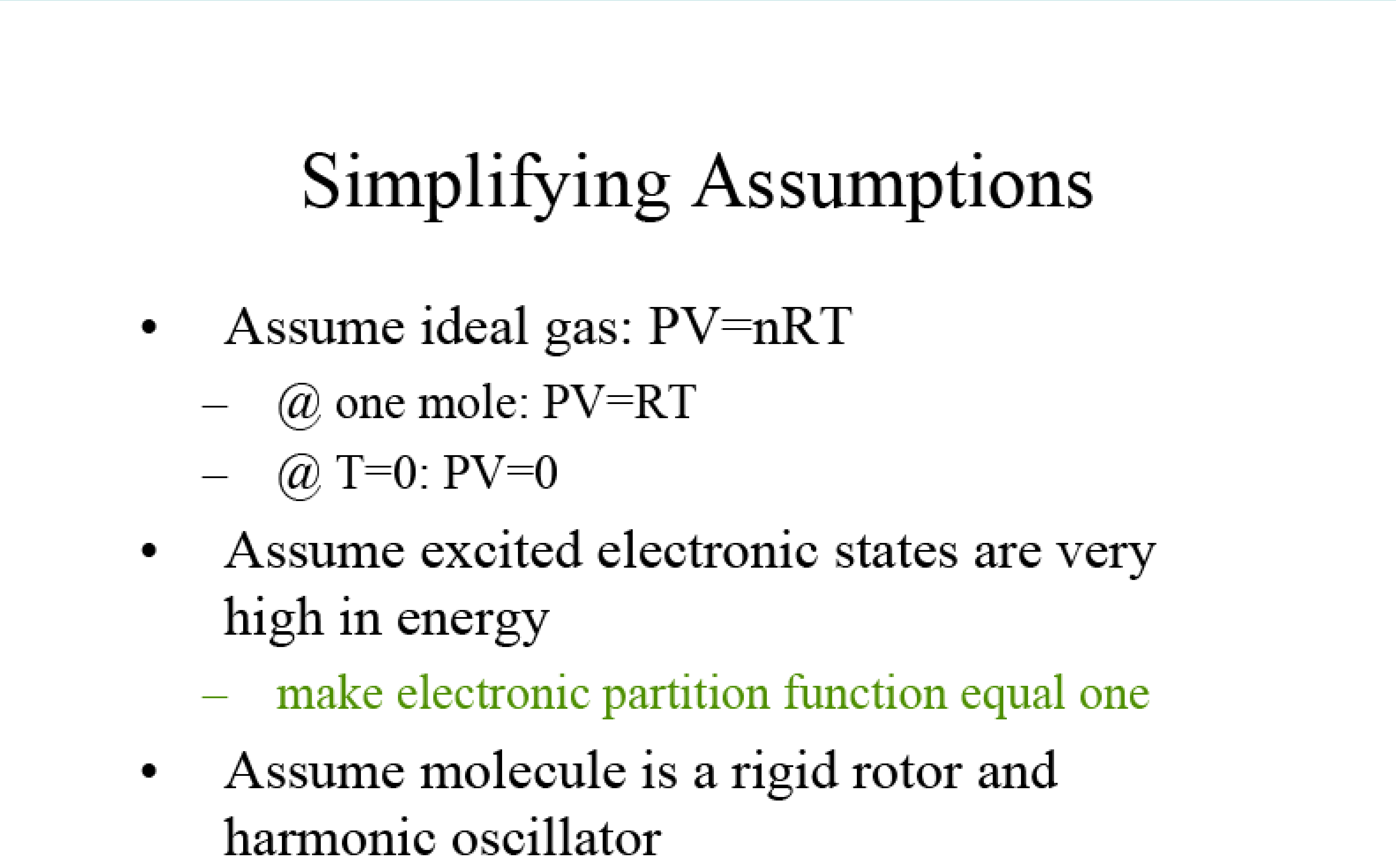
Translational kinetic energy: (dense levels, like classical system; depends only on molecular weight, *choice of standard-state volume*, and temperature; 0 at 0 K)

Rotational kinetic energy: (if rigid rotator: dense levels, like classical system; depends only on principal moments of inertia and temperature; 0 at 0 K)

Vibrational kinetic energy: (if harmonic oscillator: *not* dense levels, but convergent sum; depends only on molecular vibrational frequencies (normal modes) and temperature; *not* 0 at 0 K for QMHO)

Practically geometry and vibrational frequencies are all that required to do thermodynamical calculations

Zero-point vibrational energy (ZPVE)



Simplifying Assumptions

- Assume ideal gas: PV=nRT
  - @ one mole: PV=RT
  - @ T=0: PV=0
- Assume excited electronic states are very high in energy
  - make electronic partition function equal one
- Assume molecule is a rigid rotor and harmonic oscillator

Ideal gas assumption allows to get Q(N,V,T) in terms of q(V,T)

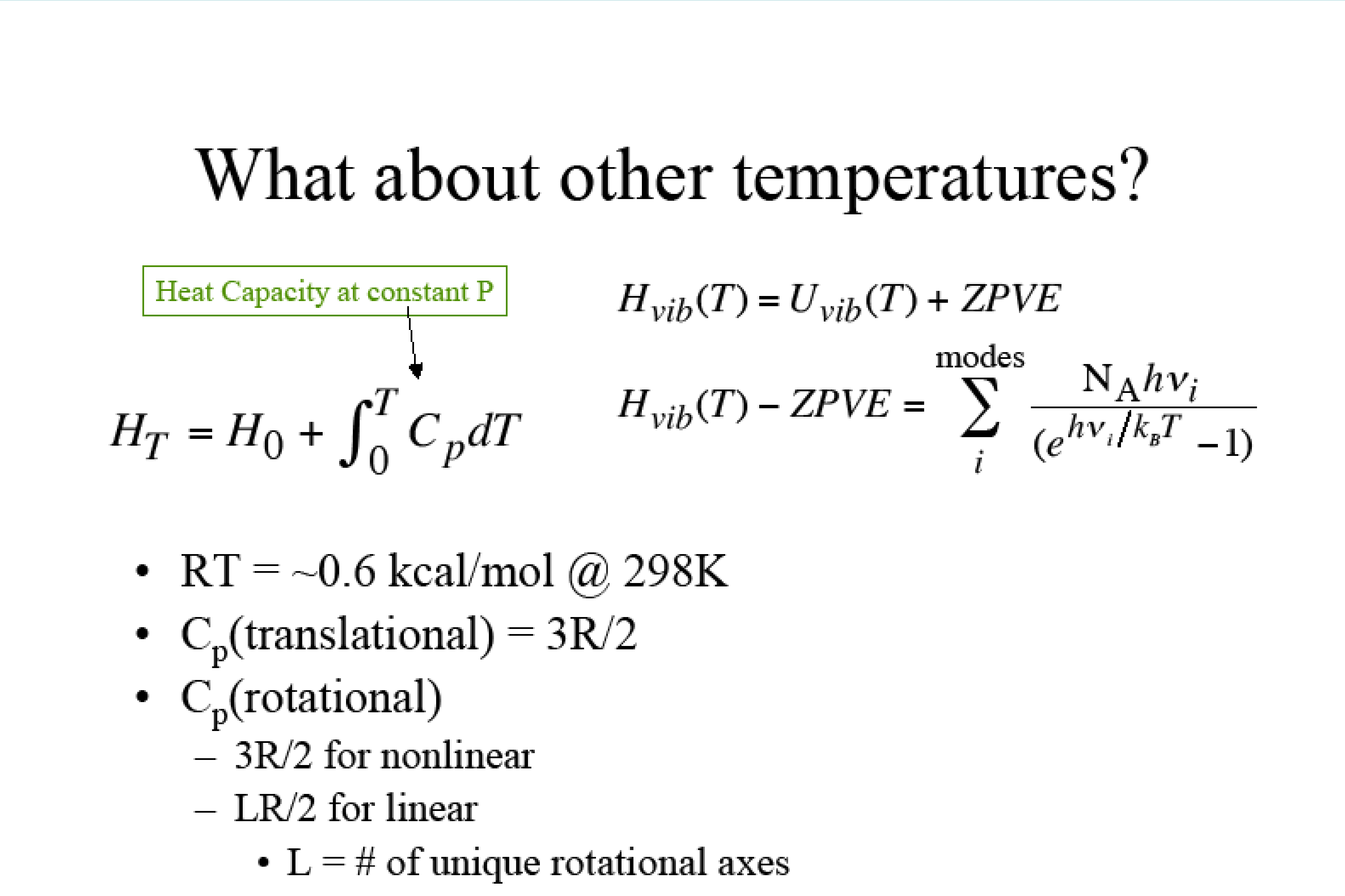
$$Q(N,V,T) = \frac{[q(V,T)]^N}{N!}$$

Normal modes

Now the Electronic: $$U_0 = E_0 + \underbrace{\frac{1}{2}h\sum_{i}^{\text{modes}}\nu_i}_{\text{Zero Point Vibrational Energy}}$$

Enthalpy at T=0 K

$$H_0 = U_0 = E_0 + \frac{1}{2}h\sum_{i}^{\text{modes}}\nu_i$$



What about other temperatures?

Heat Capacity at constant P

$$H_T = H_0 + \int_0^T C_p dT$$

$$H_{vib}(T) = U_{vib}(T) + ZPVE$$

$$H_{vib}(T) - ZPVE = \sum_i^{\text{modes}} \frac{\mathrm{N_A} h\nu_i}{(e^{h\nu_i/k_B T} - 1)}$$

- RT = ~0.6 kcal/mol @ 298K
- C_p(translational) = 3R/2
- C_p(rotational)
  - – 3R/2 for nonlinear
  - – LR/2 for linear
    - L = # of unique rotational axes

$$H_{vib}(T) - ZPVE = \sum_{i}^{\text{modes}} \frac{\mathrm{N_A} h\nu_i}{(e^{h\nu_i/k_BT} - 1)}$$

Expand the exponential

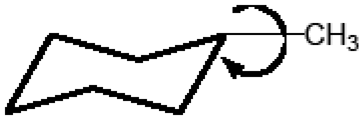
$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots \quad \text{where } x = \frac{h\nu_i}{k_BT}$$

In chemistry, frequencies rarely go to zero

$$\text{As } \nu_i \to 0 \text{ then } \quad = \sum_{i}^{\text{modes}} \frac{N_A h\nu_i}{h\nu_i/k_BT} \approx \mathrm{RT}$$

Least harmonic type of mode

$\nu = 30\ \mathrm{cm}^{-1}$



Hindered rotor → 1/2RT as ν → 0

Go in after the fact and correct

Entropy

$$S^0 = S^0_{trans} + S^0_{rot} + S^0_{vib} + S^0_{elec} - \mathrm{R}\ln \mathrm{N_A} + \mathrm{R}$$

$$S_{trans} = \mathrm{R}\left\{ \tfrac{3}{2} + \ln\left[\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{RT}{P} \right) \right] \right\}$$

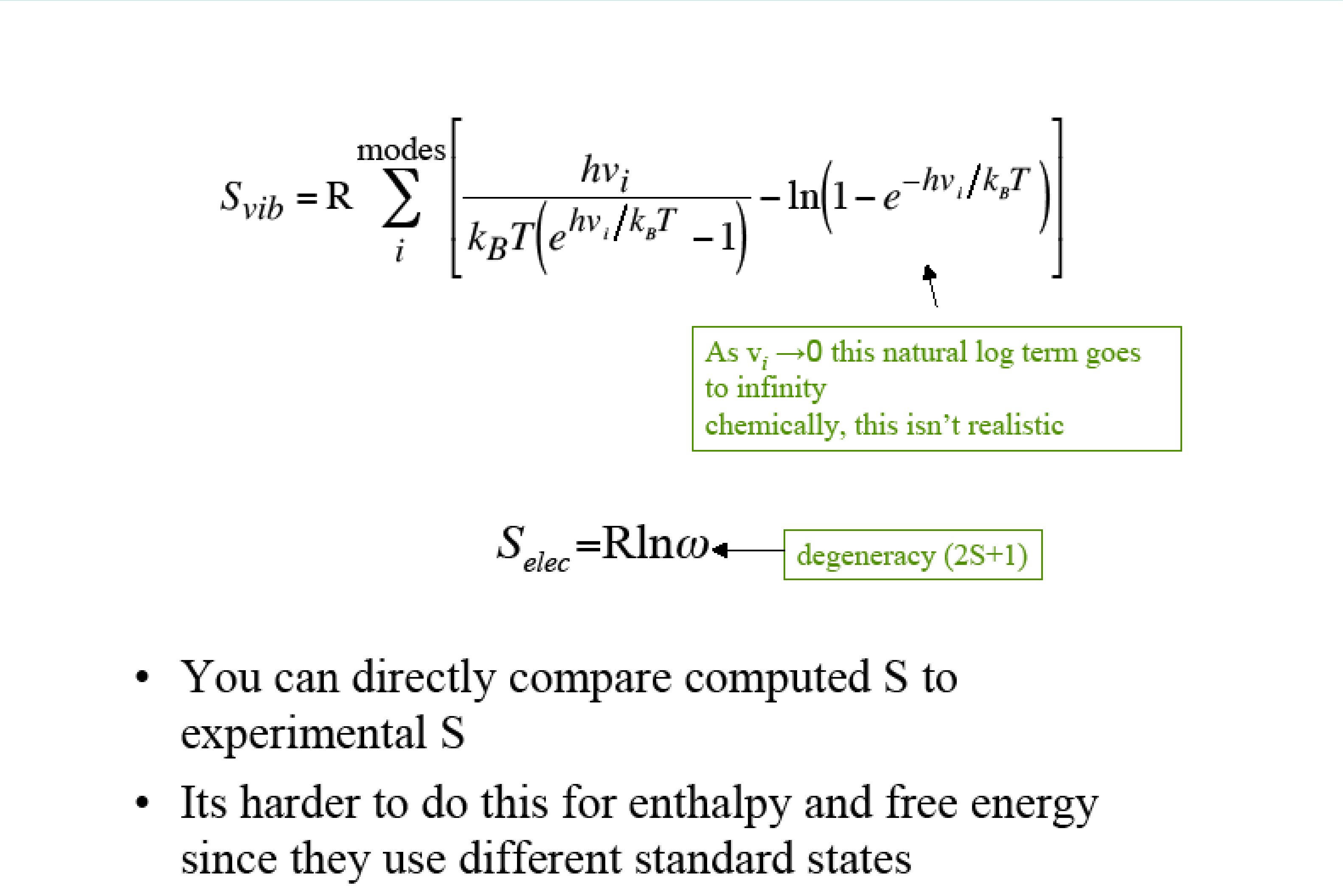
Volume term depends on standard state

Moments of Inertia

(nonlinear)

$$S_{rot} = \mathrm{R}\left\{ \tfrac{3}{2} + \ln\left[\frac{(\pi I_A I_B I_C)^{1/2}}{\sigma} \left(\frac{8\pi^2 m k_B T}{h^2} \right)^{3/2} + \tfrac{3}{2} \right] \right\}$$

Symmetry number



$$S_{vib} = \mathrm{R}\sum_{i}^{\text{modes}}\left[\frac{h\nu_i}{k_B T\left(e^{h\nu_i/k_BT}-1\right)} - \ln\left(1-e^{-h\nu_i/k_BT}\right)\right]$$

As $\nu_i \rightarrow 0$ this natural log term goes to infinity
chemically, this isn't realistic

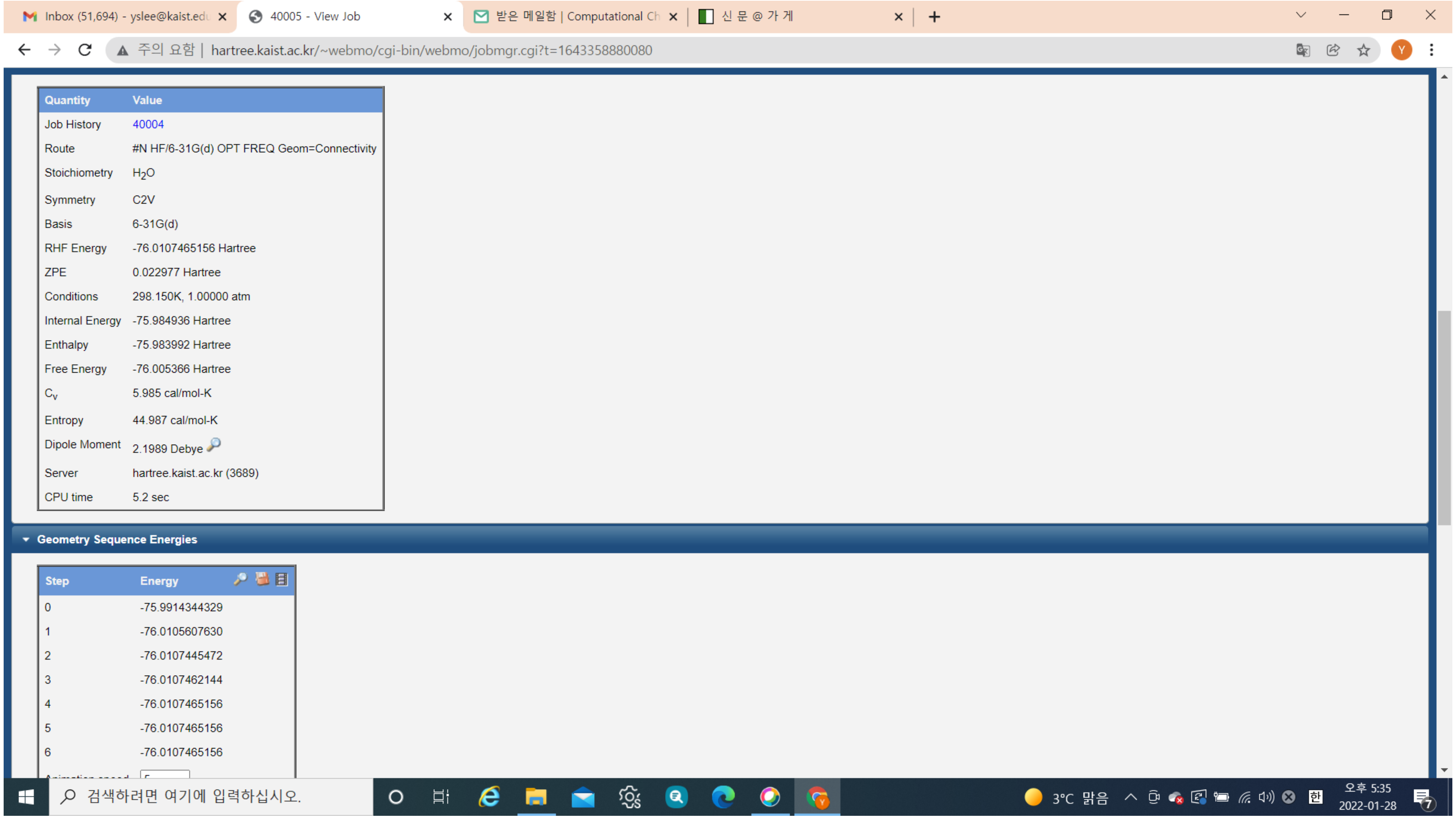
$$S_{elec} = \mathrm{R}\ln\omega$$

degeneracy (2S+1)

- You can directly compare computed S to experimental S
- Its harder to do this for enthalpy and free energy since they use different standard states

Practical Thermodynamics (No Equations)

- Ground-state electronic degeneracy, mass, optimized geometry, and vibrational frequencies are all that is required to compute ideal-gas thermodynamic quantities
- Relative zero is all nuclei and electrons infinitely separated and motionless at 0 K (somewhat inconvenient in the laboratory…)
- The entropy of a harmonic oscillator becomes infinite as its frequency goes to zero, so the QMHO approximation breaks down for very low frequencies
- Entropy is an absolute quantity; computed entropies agree extraordinarily well with measured ones for gaseous molecules, so there is reason to be hopeful about other thermodynamic quantities

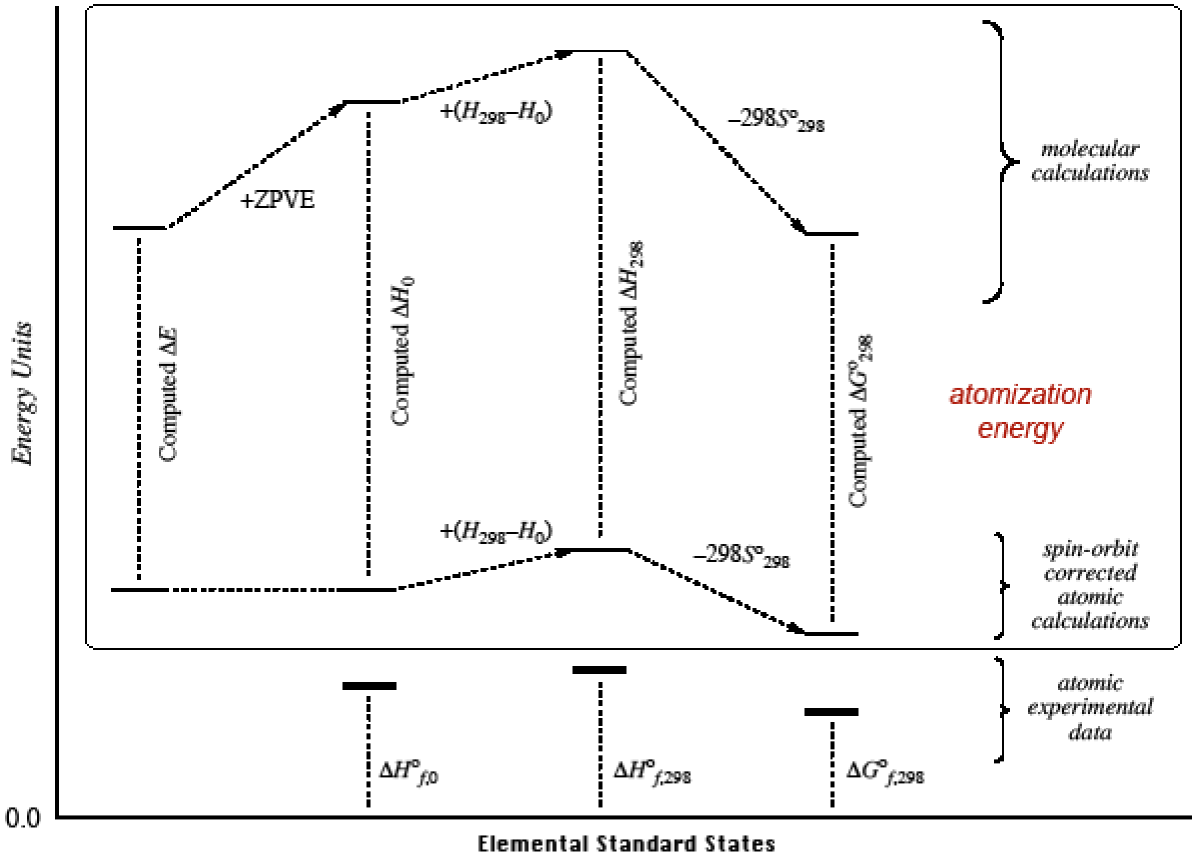


Quantity	Value
Job History	40004
Route	#N HF/6-31G(d) OPT FREQ Geom=Connectivity
Stoichiometry	H_2O
Symmetry	C2V
Basis	6-31G(d)
RHF Energy	-76.0107465156 Hartree
ZPE	0.022977 Hartree
Conditions	298.150K, 1.00000 atm
Internal Energy	-75.984936 Hartree
Enthalpy	-75.983992 Hartree
Free Energy	-76.005366 Hartree
C_v	5.985 cal/mol-K
Entropy	44.987 cal/mol-K
Dipole Moment	2.1989 Debye
Server	hartree.kaist.ac.kr (3689)
CPU time	5.2 sec

Geometry Sequence Energies

Step	Energy
0	-75.9914344329
1	-76.0105607630
2	-76.0107445472
3	-76.0107462144
4	-76.0107465156
5	-76.0107465156
6	-76.0107465156

How to Reconcile Experimental and Theoretical Standard-State Conventions?



atomization energy

Heats of Formation

- Atomization method accuracy depends on level of theory’s ability to model electron correlation
- Isodesmic reactions
- Semi-empirical methods
- Molecular Mechanics

Calculations at semiempirical levels of theory report heats of formation without ever doing frequency calculations. Explain how the predicted heat of formation is computed and what is involved in foregoing a frequency calculation.

How Do One-electron Theories Do?

G3/99 Test Set (223 Molecules)

- HF/6-311+G(3df,2p): MUE, 211.5 kcal mol^{-1}; Max, 582.2 kcal mol^{-1}
- LDA/6-311+G(2df,p): MUE, 121.9 kcal mol^{-1}; Max, 347.5 kcal mol^{-1}
- BPW91/6-311++G(3df,3pd): MUE, 9.0 kcal mol^{-1}; Max, 28.0 kcal mol^{-1}
- TPSS/6-311++G(3df,3pd): MUE, 5.8 kcal mol^{-1}; Max, 22.9 kcal mol^{-1}
- TPSSh/6-311++G(3df,3pd): MUE, 3.9 kcal mol^{-1}; Max, 16.2 kcal mol^{-1}

Hybrid DFT not bad, but still not really acceptable

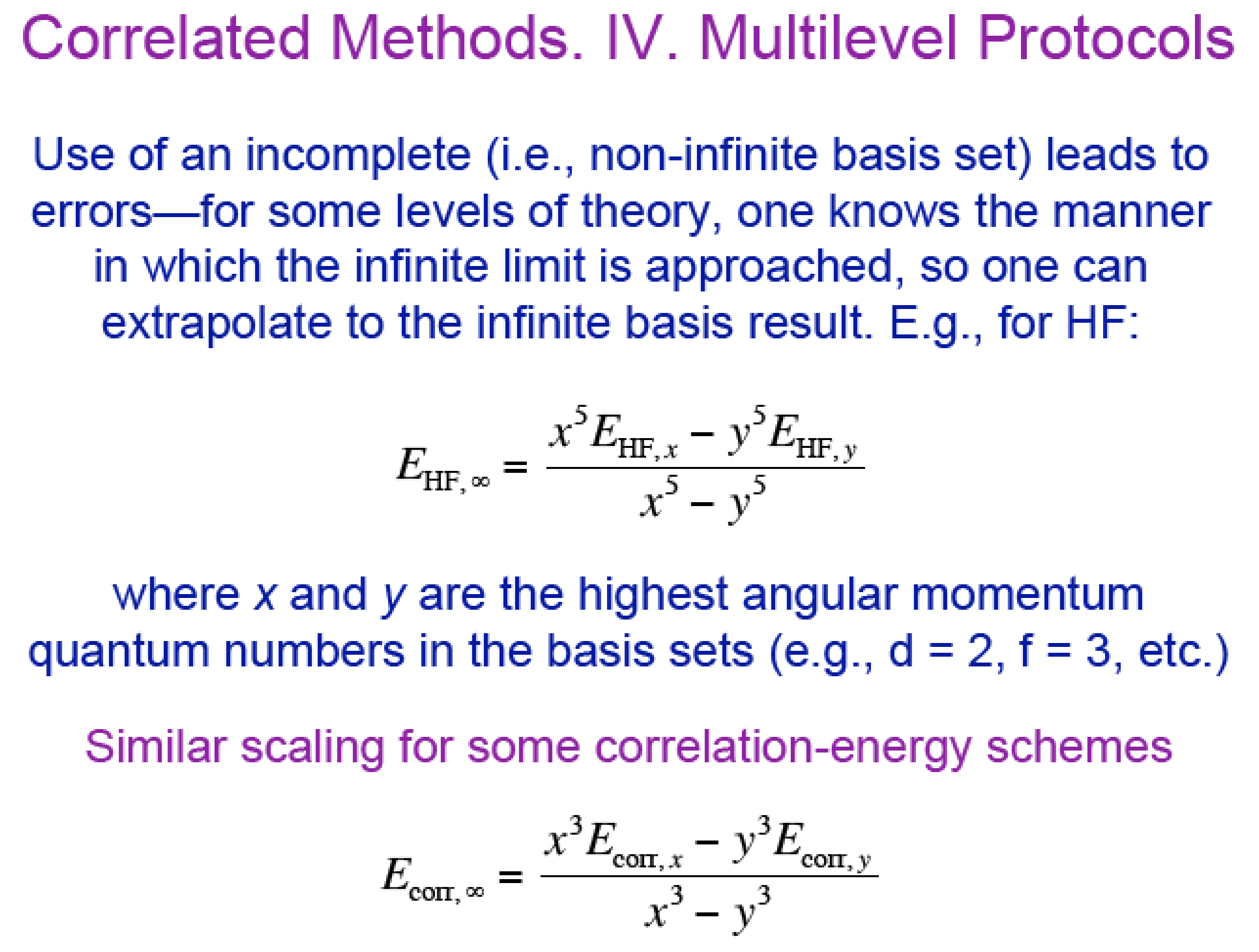
How Do Post-HF Theories Do?

Various Atomization Energy Test Sets

- HF/6-311+G(3df,2p): MUE, 211.5 kcal mol^{-1}; Max, 582.2 kcal mol^{-1}
- TPSSh/6-311++G(3df,3pd): MUE, 3.9 kcal mol^{-1}; Max, 16.2 kcal mol^{-1}
- MP2/6-311+G(3df,2p): MUE, 9.7 kcal mol^{-1}; Max, ~25 kcal mol^{-1}
- QCISD/6-31G(d): MUE, 51.7 kcal mol^{-1} (109 molecules)
- CCSD(T)/6-311G(2df,p): MUE, 11.5 kcal mol^{-1} (32 molecules)

Great theories, maybe, but disastrous thermochemistry

Mulitilevel protocol sometimes aims at thermochemistry



Correlated Methods. IV. Multilevel Protocols

Use of an incomplete (i.e., non-infinite basis set) leads to errors—for some levels of theory, one knows the manner in which the infinite limit is approached, so one can extrapolate to the infinite basis result. E.g., for HF:

$$E_{\mathrm{HF},\infty} = \frac{x^5 E_{\mathrm{HF},x} - y^5 E_{\mathrm{HF},y}}{x^5 - y^5}$$

where *x* and *y* are the highest angular momentum quantum numbers in the basis sets (e.g., d = 2, f = 3, etc.)

Similar scaling for some correlation-energy schemes

$$E_{\mathrm{corr},\infty} = \frac{x^3 E_{\mathrm{corr},x} - y^3 E_{\mathrm{corr},y}}{x^3 - y^3}$$

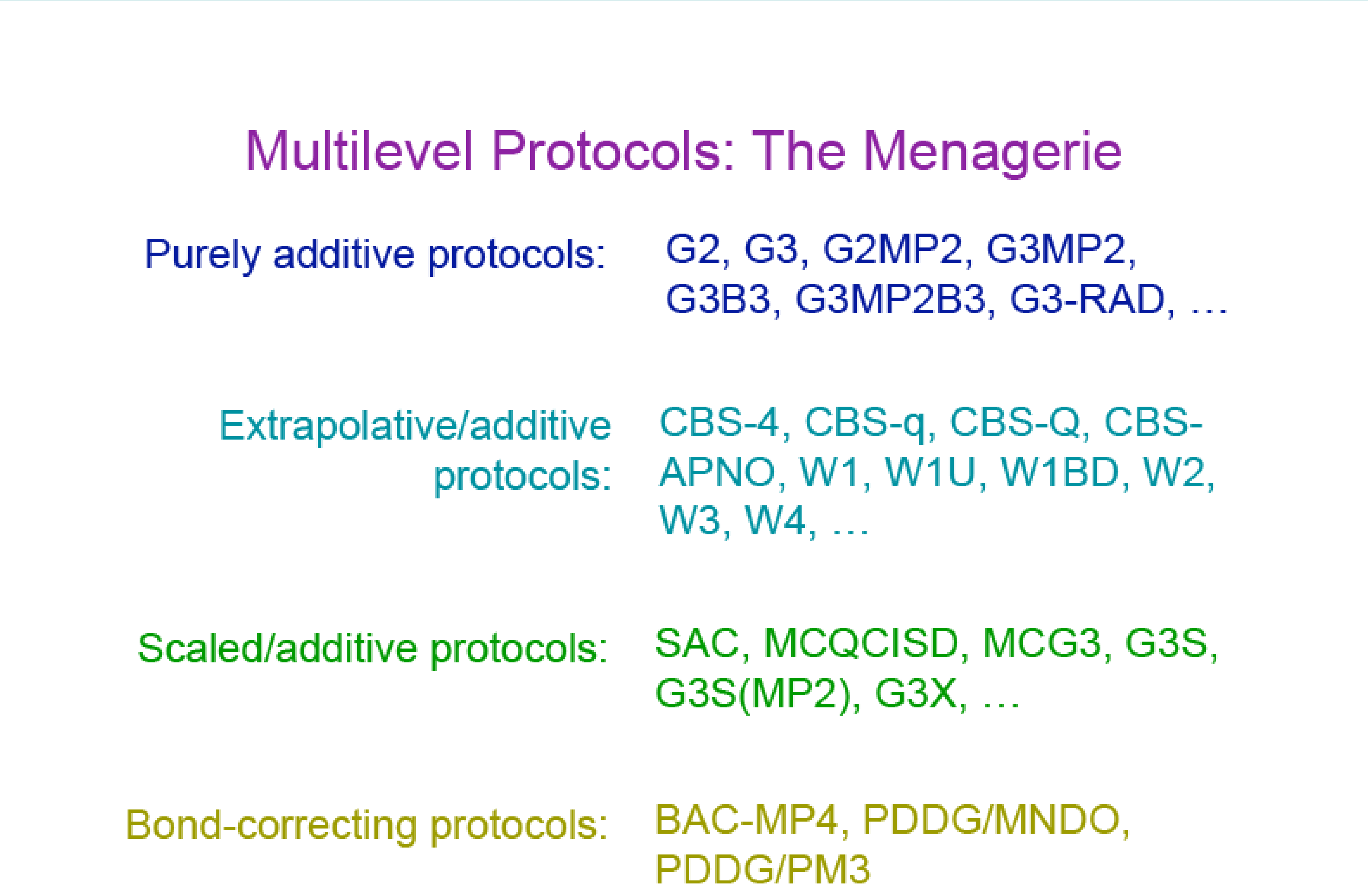
Multilevel Protocols: Tema y Variaciones

Rather than estimating limits in a rigorous fashion, consider total energy to be a linear combination of components with empirically optimized coefficients

$$E_{\text{multilevel}} = \sum_{i}^{\text{components}} c_i \varepsilon_i$$

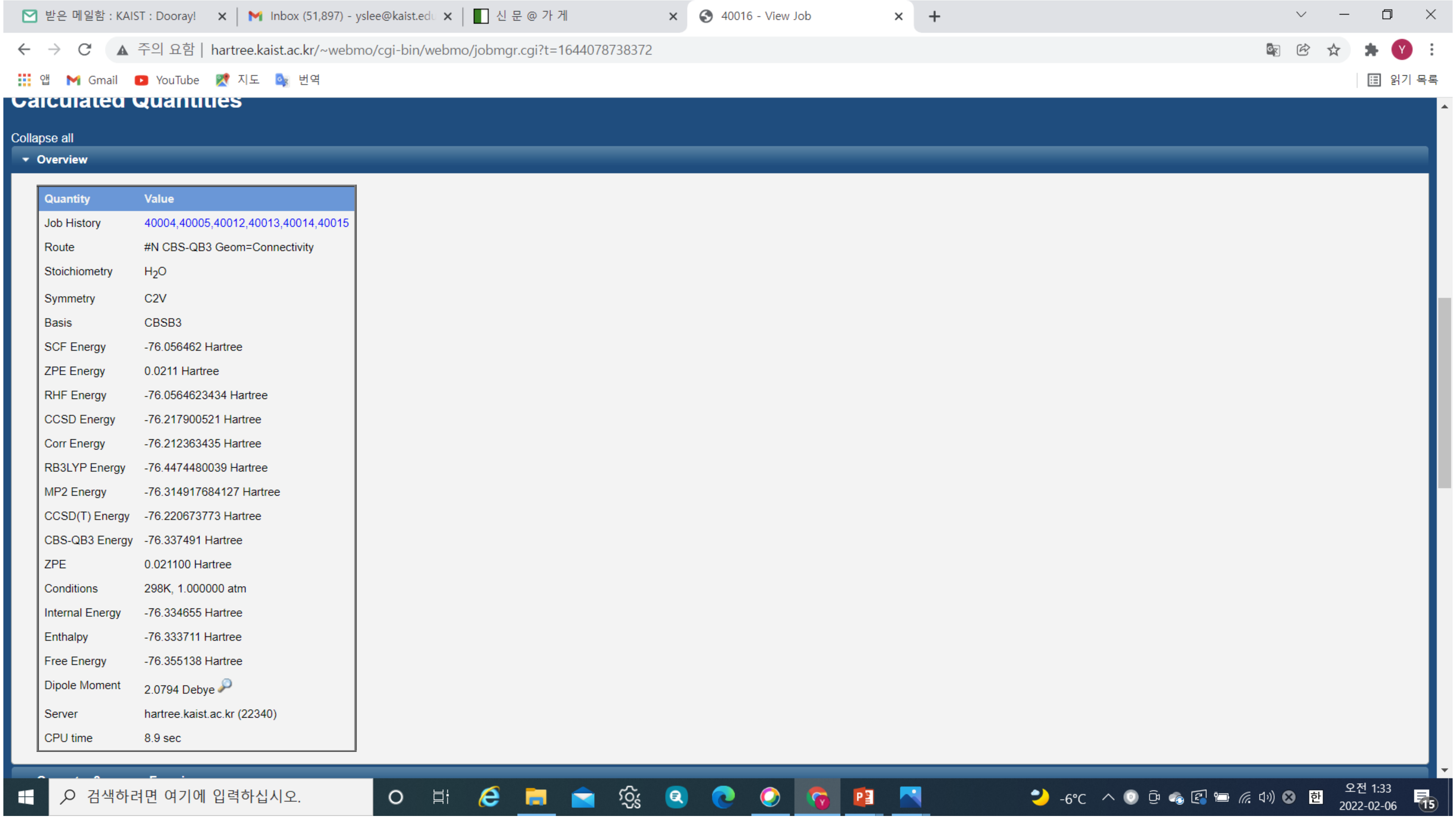
ε_1	MP2/cc-pVDZ (optimized structure *a*)
ε_2	MP2/aug-cc-pVTZ – MP2/cc-pVDZ // *a*
ε_3	MP4/cc-pVTZ – MP2/cc-pVDZ // *a*
ε_4	CCSD(T)/cc-pVDZ – MP4/cc-pVDZ // *a*
ε_5	etc. (possible empirical terms)

may also include scaled thermochemical contributions, of course



Multilevel Protocols: The Menagerie

Purely additive protocols:	G2, G3, G2MP2, G3MP2, G3B3, G3MP2B3, G3-RAD, …
Extrapolative/additive protocols:	CBS-4, CBS-q, CBS-Q, CBS-APNO, W1, W1U, W1BD, W2, W3, W4, …
Scaled/additive protocols:	SAC, MCQCISD, MCG3, G3S, G3S(MP2), G3X, …
Bond-correcting protocols:	BAC-MP4, PDDG/MNDO, PDDG/PM3



Calculated Quantities

Collapse all

Overview

Quantity	Value
Job History	40004,40005,40012,40013,40014,40015
Route	#N CBS-QB3 Geom=Connectivity
Stoichiometry	H_2O
Symmetry	C2V
Basis	CBSB3
SCF Energy	-76.056462 Hartree
ZPE Energy	0.0211 Hartree
RHF Energy	-76.0564623434 Hartree
CCSD Energy	-76.217900521 Hartree
Corr Energy	-76.212363435 Hartree
RB3LYP Energy	-76.4474480039 Hartree
MP2 Energy	-76.314917684127 Hartree
CCSD(T) Energy	-76.220673773 Hartree
CBS-QB3 Energy	-76.337491 Hartree
ZPE	0.021100 Hartree
Conditions	298K, 1.000000 atm
Internal Energy	-76.334655 Hartree
Enthalpy	-76.333711 Hartree
Free Energy	-76.355138 Hartree
Dipole Moment	2.0794 Debye
Server	hartree.kaist.ac.kr (22340)
CPU time	8.9 sec

How Do Multilevel Protocols Do?

Various Atomization Energy Test Sets

- TPSSh/6-311++G(3df,3pd): MUE, 3.9 kcal mol^{-1}; Max, 16.2 kcal mol^{-1}
- MP2/6-311+G(3df,2p): MUE, 9.7 kcal mol^{-1}; Max, ~25 kcal mol^{-1}
- CBS-Q: MUE, 1.2 kcal mol^{-1}; Max, 8.1 kcal mol^{-1}
- G3: MUE, 1.1 kcal mol^{-1}; Max, 7.1 kcal mol^{-1}
- W2: MUE, 0.5 kcal mol^{-1}; Max, 1.9 kcal mol^{-1} (55 molecules—wildly expensive)

What’s the Right Way to Do a Calculation?

- Solve the Schrödinger equation exactly (full CI, infinite basis)—rarely practical…
- Use a multilevel approach to get as close as you can to the exact solution
- Use an isodesmic protocol to foster error cancellation
- Assume error transferability between related known and unknown systems at an affordable level
- Assume that good results for a known property of the system will ensure good results for an unknown

- Indulge in optimism and hope

계산양자화학의 장래

- 이론 및 방법 개발
  - 컴퓨터 발달 방향에 따라 완전히 새로운 계산법 도입 필요 기대 (양자 컴퓨터등)
  - 연구의 필요성 증가 그러나 과제에 비해 과학자의 수요는 대학, 기초분야연구소등에 머물듯
  - 이 분야 학위 취득자의 증가, 타분야로 진출
  - MO 이론 혹은 양자역학을 뛰어 넘는 새로운 이론의 출현?
  - 인공지능, 기계학습의 접목 (QSPR 확장)

- 양자화학 계산응용
  - 양자화학 계산이 분석 도구로 정착. 보편적 실험도구로 인식됨
  - Modeling and Simulation 의 주요 도구로 multi-scale simulation의 단골 메뉴로 발전
  - 소재분야, 생물 분야에서의 응용 확산
  - 계산화학 기법이 거의 모든 실험기기의 주요 부분이 됨.

- **너무 성공적이어서 독립학문분야에서 벗어날 수도**

KAIST