Møller-Plesset Perturbation Theory

$$E_{\mathrm{MP2,c}} = -\frac{1}{4}\sum_{a<b}^{\mathrm{occ}}\sum_{r<s}^{\mathrm{virt}} \frac{|\langle ab||rs\rangle|^2}{\varepsilon_r + \varepsilon_s - \varepsilon_a - \varepsilon_b}$$

- Include correlation as perturbation up to order n
  - Zeroth order is Hartree-Fock
- Does not necessarily converge (or behave well)
- Comparably simple method, common for weak correlation
- Higher orders possible, yet much more expensive and not quite better
- Yields energies, no new wave functions, not variational, size-consistent

Coupled Cluster

$$\Psi_{\mathrm{CCSD}} = \exp(\hat{T}_1 + \hat{T}_2)\Psi_{\mathrm{HF}}$$

$$\hat{T}_1 = \sum_{a}^{\mathrm{occ}} \sum_{r}^{\mathrm{vir}} t_a^r \hat{a}_r^\dagger \hat{a}_a$$

$$\hat{T}_2 = \frac{1}{4} \sum_{ab}^{\mathrm{occ}} \sum_{rs}^{\mathrm{vir}} t_{ab}^{rs} \hat{a}_r^\dagger \hat{a}_s^\dagger \hat{a}_a \hat{a}_b$$

- T_1 are all single excitations, T_2 all double, …
- Taylor expansion of exp yields combinations and relation between amplitudes *t* and FCI coefficients *c*
- Rearrange all terms from FCI, formally equivalent if all excitations would be included
- Common variants: CCSD (singles doubles), CCSD(T) (singles doubles with perturbative triples)
- Methods beyond CCSD(T) are rare
- CCSD(T) is often called the “gold standard” for weak correlation
- Yields energies, new wave function, not variational, size consistent

MRCC

Computational complexity

Depends on number of basis functions n (ignoring screening & implementation tricks for now)

DFT	$O(n^3)$
HF	$O(n^4)$
MP2	$O(n^5)$
MP3	$O(n^6)$
MP4	$O(n^7)$
CCSD	$O(n^6)$
CCSD(T)	$O(n^7)$
CCSDT	$O(n^8)$
CCSDTQ	$O(n^{10})$
FCI	$O(n!)$

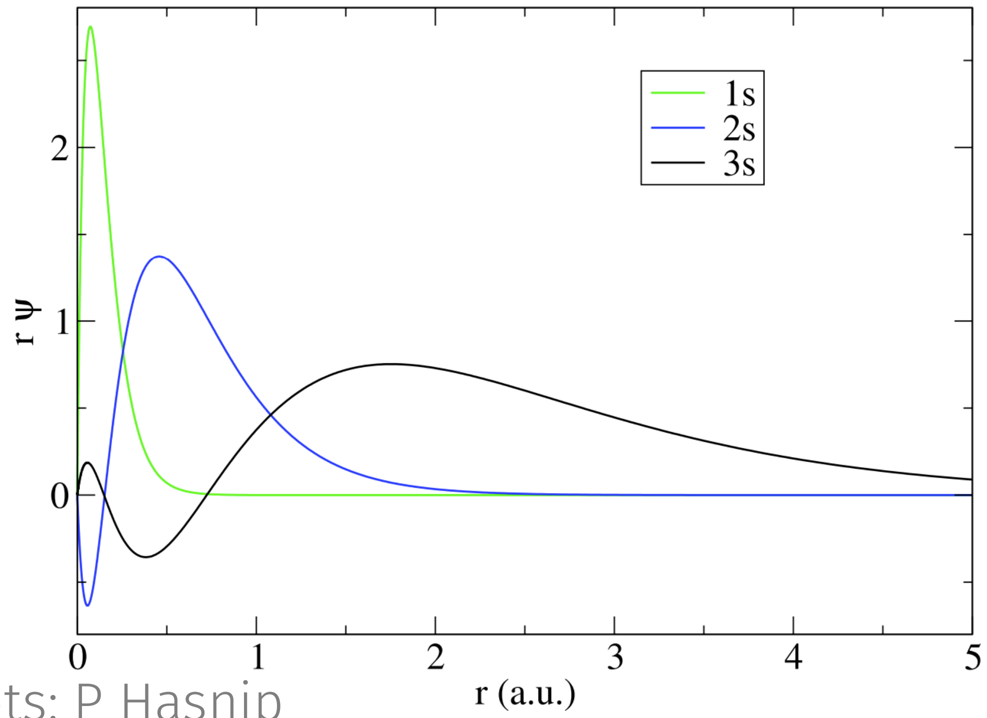
Pseudopotentials

Core Idea

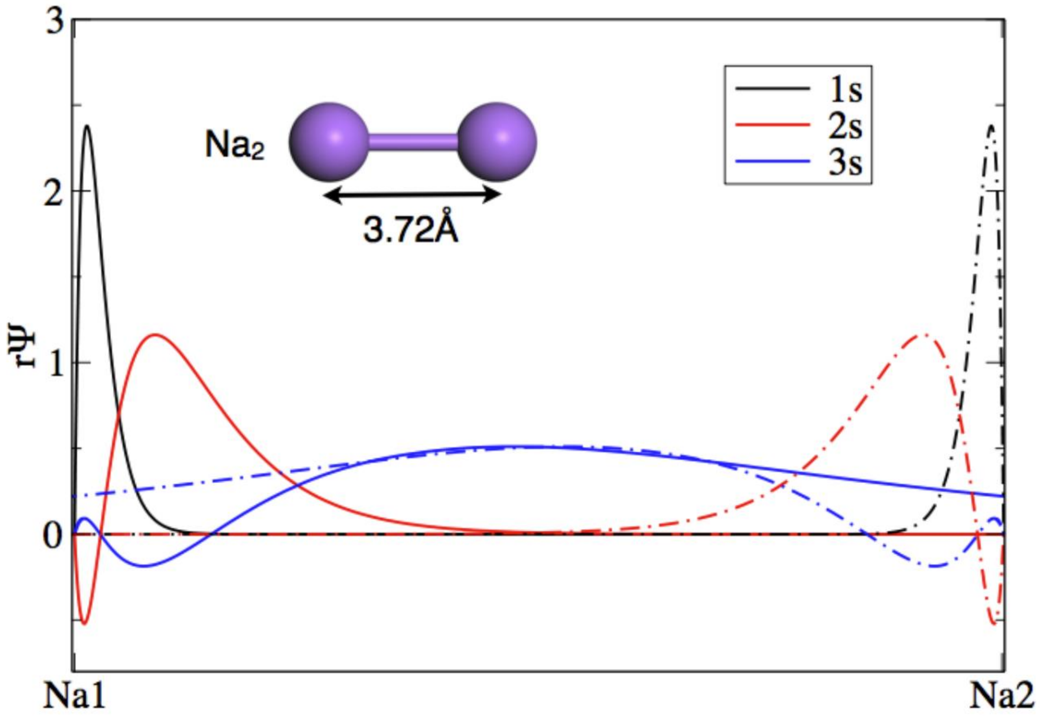
- Core electrons are rarely affected by bonding and do not overlap between atoms
- Core wavefunctions are highly localised
  - Expensive in plane waves

What if the core is isolated and imputed/precomputed?

Atomic sodium



Sodium dimer



Plots: P Hasnip

Frozen Core

- Core electrons stay as they are, no response to environment
- The opposite: “all-electron calculation”
- Implicit default in many calculations, little impact on geometries
- Requires special basis sets to turn off: e.g. cc-pVnZ ->cc-pCVnZ
- Somewhat arbitrary separation into core/valence
- ORCA:

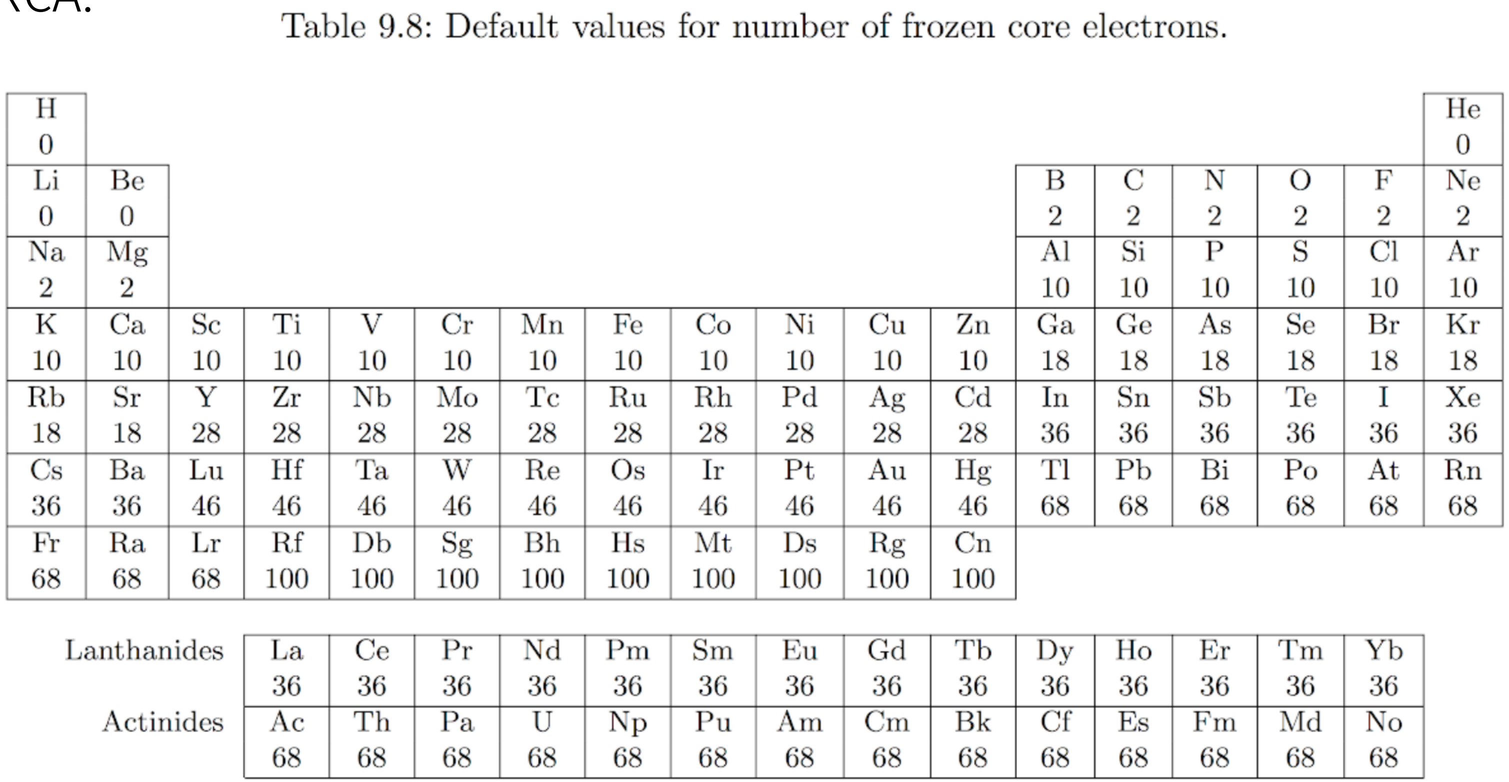
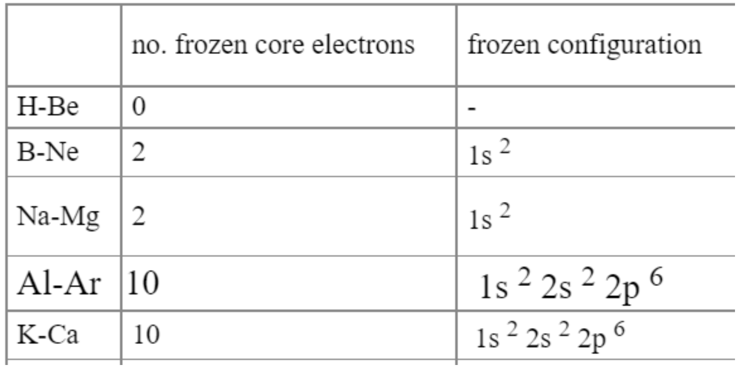


Table 9.8: Default values for number of frozen core electrons.

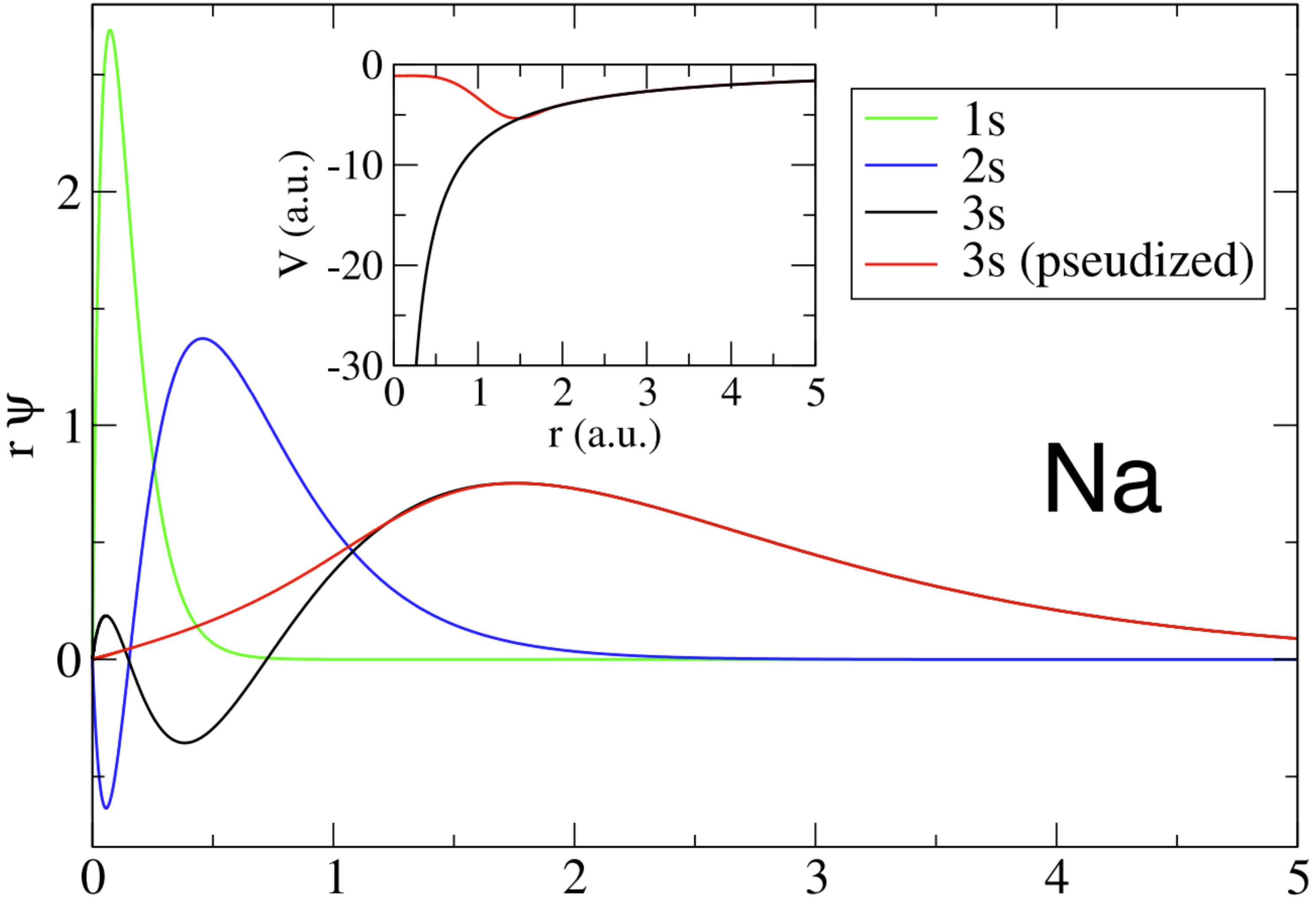
H 0																	He 0
Li 0	Be 0											B 2	C 2	N 2	O 2	F 2	Ne 2
Na 2	Mg 2											Al 10	Si 10	P 10	S 10	Cl 10	Ar 10
K 10	Ca 10	Sc 10	Ti 10	V 10	Cr 10	Mn 10	Fe 10	Co 10	Ni 10	Cu 10	Zn 10	Ga 18	Ge 18	As 18	Se 18	Br 18	Kr 18
Rb 18	Sr 18	Y 28	Zr 28	Nb 28	Mo 28	Tc 28	Ru 28	Rh 28	Pd 28	Ag 28	Cd 28	In 36	Sn 36	Sb 36	Te 36	I 36	Xe 36
Cs 36	Ba 36	Lu 46	Hf 46	Ta 46	W 46	Re 46	Os 46	Ir 46	Pt 46	Au 46	Hg 46	Tl 68	Pb 68	Bi 68	Po 68	At 68	Rn 68
Fr 68	Ra 68	Lr 68	Rf 100	Db 100	Sg 100	Bh 100	Hs 100	Mt 100	Ds 100	Rg 100	Cn 100						

Lanthanides	La 36	Ce 36	Pr 36	Nd 36	Pm 36	Sm 36	Eu 36	Gd 36	Tb 36	Dy 36	Ho 36	Er 36	Tm 36	Yb 36
Actinides	Ac 68	Th 68	Pa 68	U 68	Np 68	Pu 68	Am 68	Cm 68	Bk 68	Cf 68	Es 68	Fm 68	Md 68	No 68



	no. frozen core electrons	frozen configuration
H-Be	0	-
B-Ne	2	$1s^2$
Na-Mg	2	$1s^2$
Al-Ar	10	$1s^2 2s^2 2p^6$
K-Ca	10	$1s^2 2s^2 2p^6$

Pseudopotential



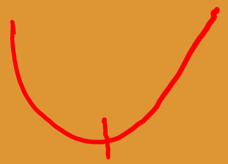
Pseudopotentials

- Away from the nuclei (outside the cutoff), all-electron and pseudo-wave function need to agree
  - All-electron wave function comes from a reference calculation
- Spectrum of Hamiltonian needs to be identical
- Pseudopotential needs to have the same effect on valence electrons
- Replaces interactions with core electrons (XC, Hartree)

Families:

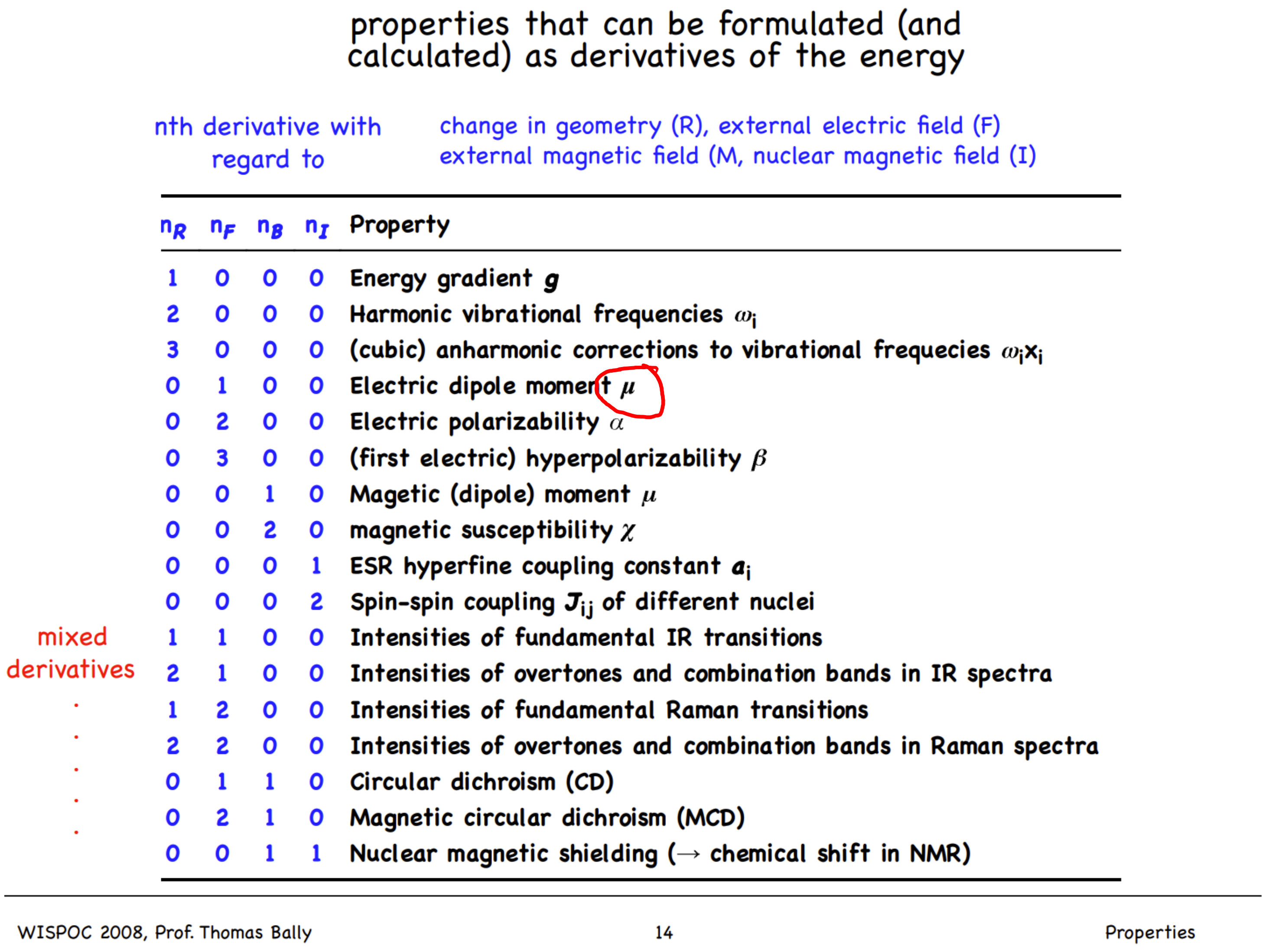
- Norm-conserving
  - Total charge until cutoff identical
- Ultrasoft

  Vanderbilt
  - Charge close to cores augmented after the fact
    - Correction depends on actual geometry
  - Cheaper for plane waves



Derivatives

Relevance of derivatives



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
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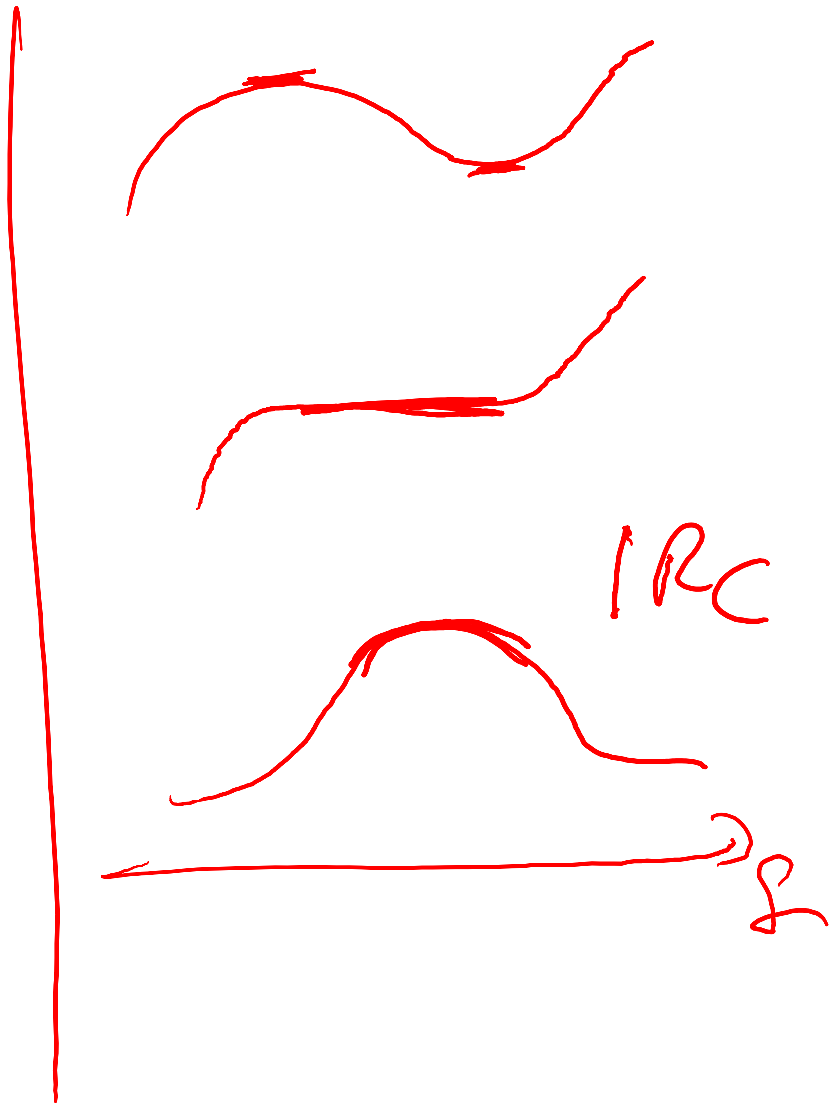
WISPOC 2008, Prof. Thomas Bally 14 Properties



Derivatives in Chemistry

Equivalents
- f(x): total energy $E(\mathbf{R}_i, Z_i)$

Gradients
- Molecular forces
    - Commonly implemented
    - Special derivations
- Alchemical derivatives: electronic electrostatic potential

Hessians
- Normal modes
    - Commonly only for spatial derivatives
    - Special derivations (less often)

What if we have no derivatives?

Finite differences (FD)

Approximative derivatives
- Similar to the limit expression

Variants
- Forward/backward
- Central
- Higher-order

Issues
- Finite displacement
- Numerical stability / finite precision
- Many calculations

Main advantage
- General applicability
- Just points and weights