An Introduction to Computational Chemistry Laboratory

Semester B, 2023

Modern Computational Chemistry - super-important and broad-ranged

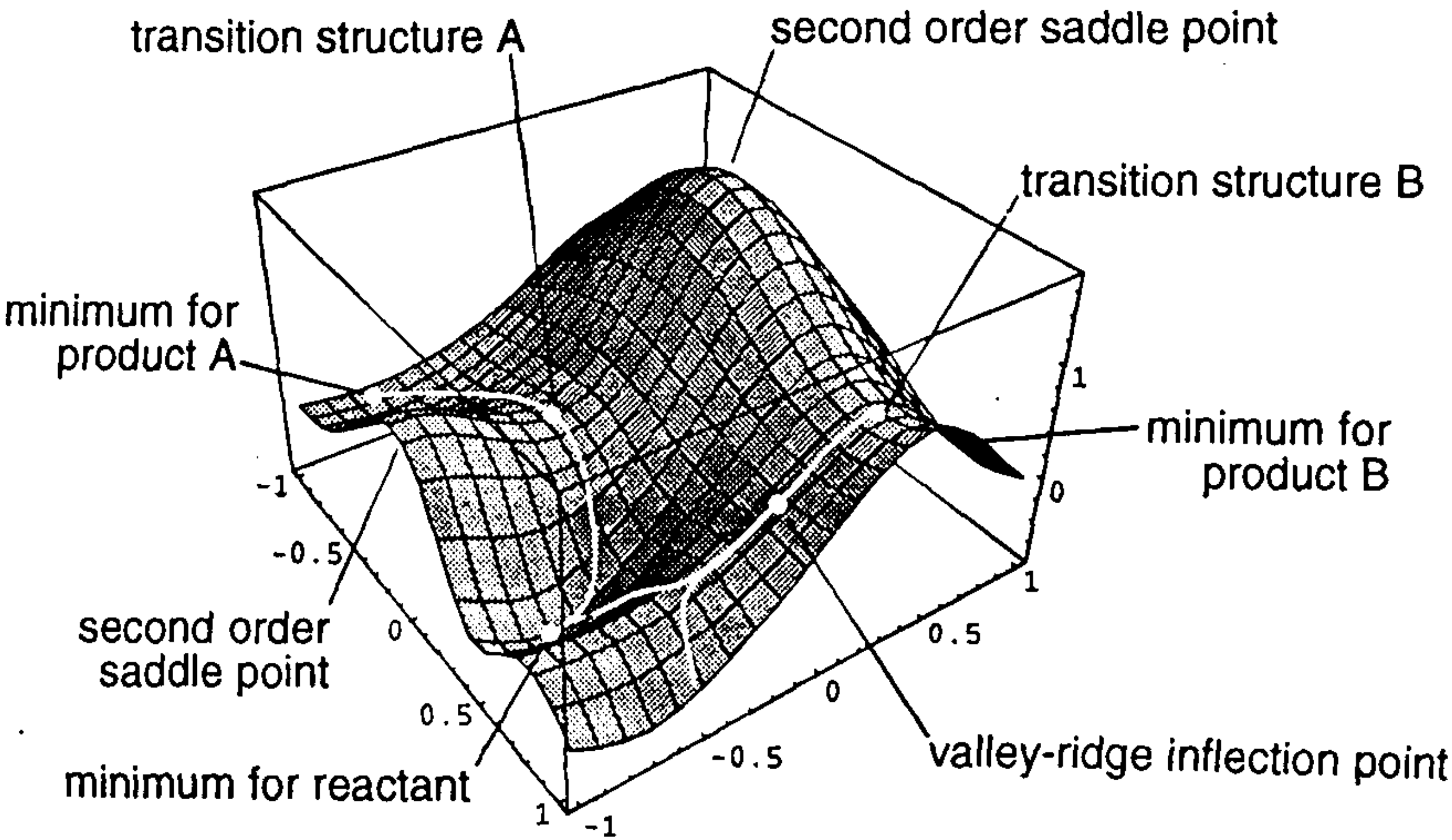
- CC is a well developed mathematically and numerically (analytical form of interactions + vast experimental data)
- CC range of applicability:
  - Chemistry: *precise structure, electronics, energetics, reactivity, kinetics and thermodynamics*
  - Physics: *fundamental physical theories beyond the Standard Model (SM) (including dark matter and energy)*
  - Biology: *live organisms molecular structure and functioning – the essential secrets of life*
  - Anthropology & AI : *from brain structure and consciousness phenomena to Artificial Intelligence (AI)*

What is Computational Chemistry Laboratory (CCL)?

- CCL is a virtual chemistry laboratory (in many cases substitutes a real laboratory….☺)
- The aim: use of computers to aid chemical inquiry. Based on:
  - Physical background theory (Classical Newtonian or Quantum Physics)
  - Mathematical numerical algorithms (optimization, linear algebra, iteration procedures, numerical integration etc.)
  - *Computer software and hardware (HYPERCHEM 8.0, GAUSSIAN03 on Windows PC)*
  - Chemical knowledge and intuition for understanding and interpretation of the computational results

Potential Energy Surface (PES) – the main chemistry inquiry

"Chemistry – is knowing the energy as a function of nuclear coordinates" F. Jensen



Potential energy surfaces (and similar properties) calculation

- **Classical (Molecular) Mechanics**
  - **quick, simple; accuracy depends on parameterization;**
  - **no consideration of electrons interaction**
- **Quantum Mechanics:**

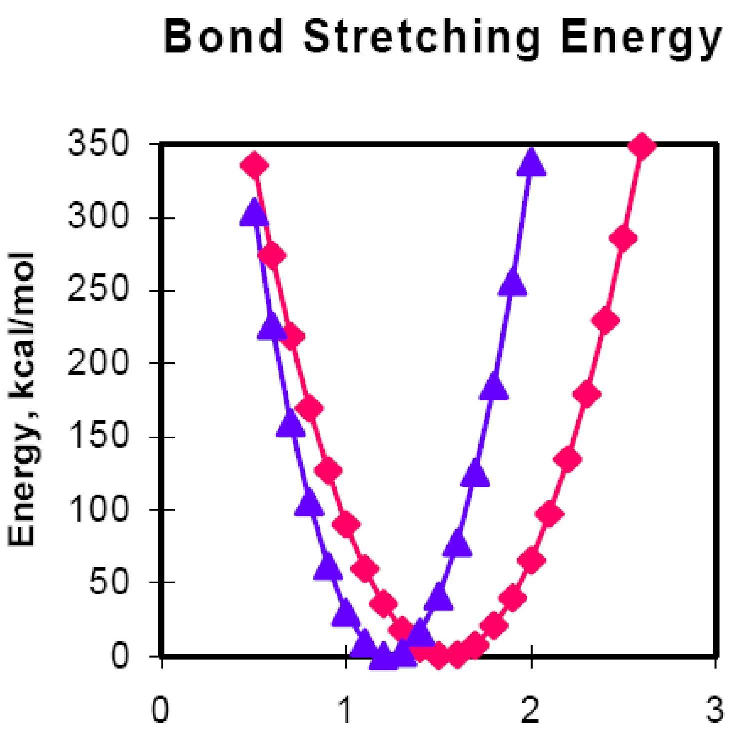
1. **Molecular Wave Function Theory**
   - ***Ab initio molecular orbital methods*...much more demanding computationally, generally more accurate.**
   - ***Semi-empirical molecular orbital methods* ...computationally less demanding than *ab initio*, possible on a pc for moderate sized molecules, but generally less accurate than *ab initio*, especially for energies.**
2. **Density functional theory… more efficient and often more accurate than Wave Function based approaches.**

Molecular Mechanics – a theory of molecules "without electrons"

- Employs classical (Newtonian) physics
- Assumes Hooke's Law forces between atoms (like a spring between two masses)

$$E_{stretch} = k_s (l - l_o)^2$$

graph: C-C; C=O



- Force field = $\{k_s, l_0\}$

Molecular Mechanics
More elaborate Force Fields (FF)

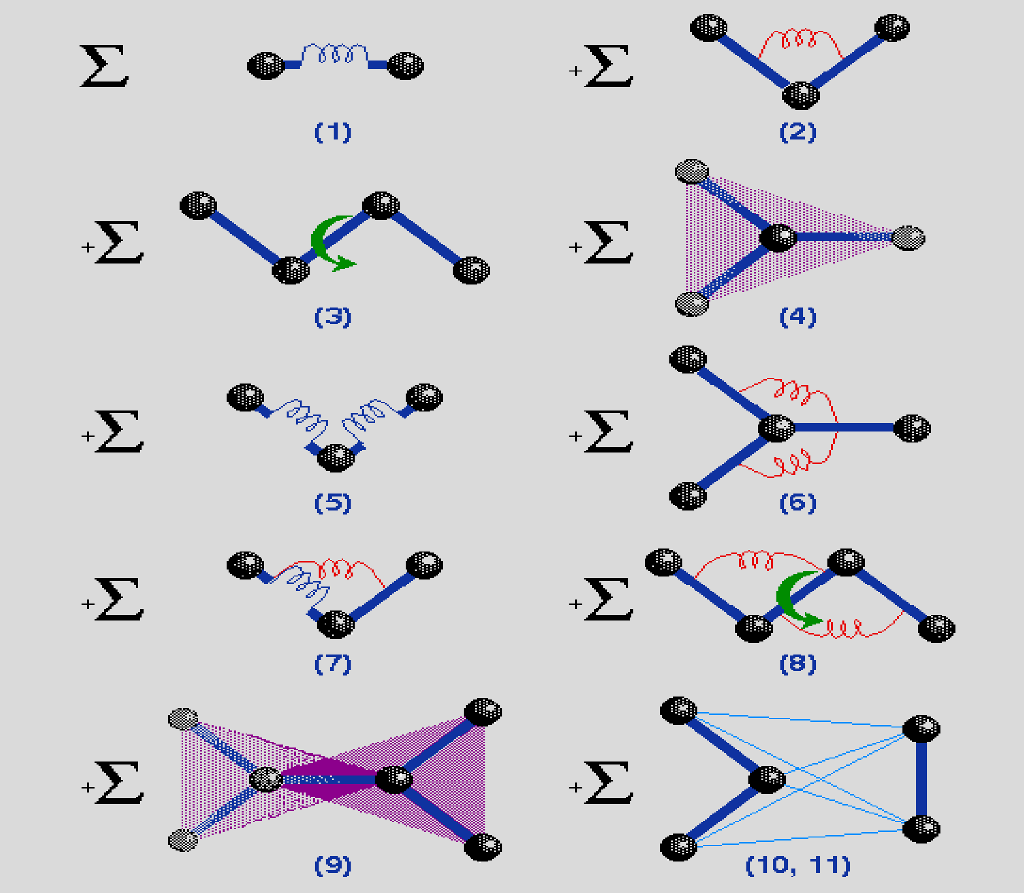


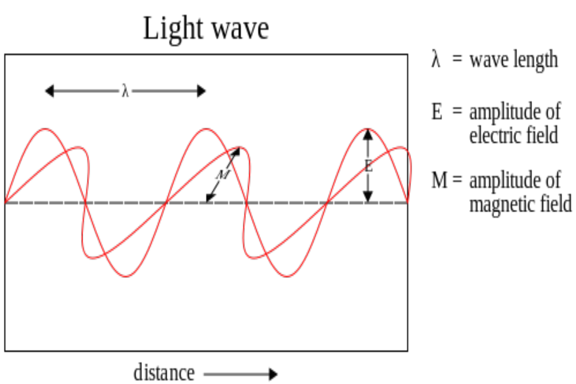
Figure 3–2. Graphic Illustration of Terms in CVFF

Birth of quantum mechanics. Matter properties of light.

14 December 1900 Planck postulated: electromagnetic energy could be emitted or adsorbed only in quantized form:

$$E=h\nu=hc/\lambda$$

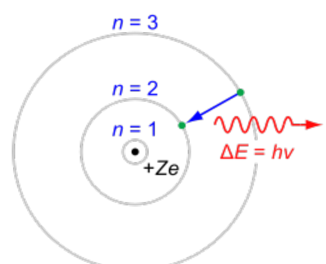
$$h= 6.62607550D^{-34}\ Js$$

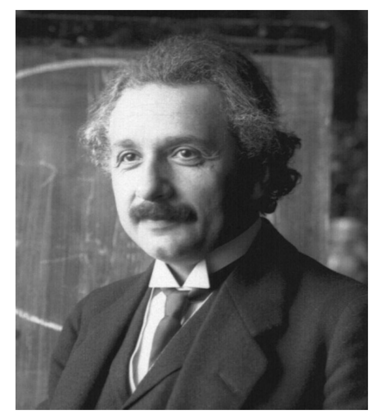


Einstein 1905:

$$E=pc$$

$$p=h/\lambda$$





Birth of quantum chemistry
Wave properties of matter

- Prince Louis de Broglie (1923):

$\lambda = h/mv = h/p$

h= 6.62607550D^{-34} Js

$\psi_p = e^{-i2\pi x/\lambda} = e^{-i2\pi px/h}$

(“wave-particle duality” paradox)

- ψ - probabilistic (statistic) wave (Copenhagen interpretation). Waves properties: interference, diffraction etc.
- **Possible explanations of the probabilistic (“quantum”) behavior**
  - **Structure of quantum vacuum.**
  - **Constrains of the human consciousness (observer’s constrains).**

Basis of Quantum Chemistry

- **Postulate I :** "A closed system is fully described by ψ"
- **Postulate II:** "Operator – for every physical quantity"

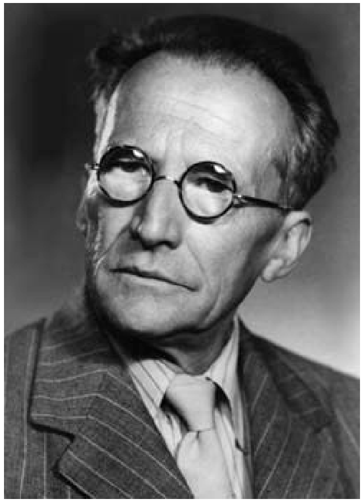
  $(-ih/2\pi)d/dx\,(e^{-i2\pi px/h}) = p\,(e^{-i2\pi px/h})$

  $(-ih/2\pi)d/dx\,(\psi_p) = p\,(\psi_p)$

  Operator – linear and Hermitian
- Schrödinger equation (1926):

$$\left(-i\hbar\frac{d\Psi}{dt}=\right)\hat{H}\Psi = E\Psi$$

(can be solved exactly for the Hydrogen atom, but nothing larger)



P.A.M. Dirac, 1929: "The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known."

One-dimensional Schrödinger wave equation

- Hamiltonian operator
  - $\hat{H}$ = operator of energy
  - SE = energy eigen-value equation
- Extracts total energy, E
- Many solutions $E_0, E_1, \ldots E_n$
- $\Psi(x)$ – wavefunction
  - No direct physical meaning
- $|\Psi(x)|^2$ – Probability of finding particle with energy E at point x
- Single-valued, finite, continuous

$$\hat{H}\psi = E\psi$$

$$\text{Total energy} = \text{kinetic} + \text{potential}$$

$$= \frac{1}{2}mv^2 + V = \frac{p^2}{2m} + V$$

$$\hat{p} = -i\hbar\left(\frac{d}{dx}\right) \quad \text{then} \quad \hat{p}^2 = \hat{p}\hat{p}$$

$$\hat{p}^2 = \left(-i\hbar\frac{d}{dx}\right)\left(-i\hbar\frac{d}{dx}\right) = -\hbar^2\frac{d^2}{dx^2}$$

$$\hat{H} \equiv -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V\psi = E\psi\left(= i\hbar\frac{d}{dt}\psi\right)$$

Molecular Schrödinger equation (SE): $\hat{H}\Psi = E\Psi$

$\hat{H}$ = Hamiltonion operator

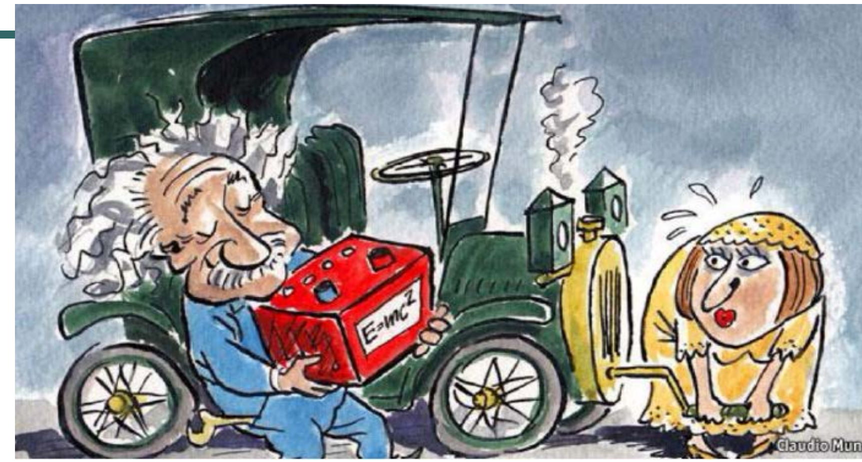
$$\hat{H} = \underbrace{-\frac{h^2}{8\pi^2}\sum_{A}^{\text{nuclei}}\frac{1}{M_A}\nabla_A^2}_{\text{kinetic energy (nuc.)}} \underbrace{-\frac{h^2}{8\pi^2 m}\sum_{a}^{\text{electrons}}\nabla_a^2}_{\text{kinetic energy (elect.)}} - e^2\sum_{A}^{\text{nuclei}}\sum_{a}^{\text{electrons}}\frac{Z_A}{r_{Aa}}$$

$$+ e^2\sum_{A}^{\text{nuclei}}\sum_{> B}\frac{Z_A Z_B}{r_{AB}} \quad + e^2\sum_{a}^{\text{electrons}}\sum_{> b}\frac{1}{r_{ab}}$$

2 kinetic energy terms plus
3 Coulombic energy terms:
(one attractive, 2 repulsive)

Relativistic effects: from the color of your wedding ring to the lead battery in your car

Silver (Ag) versus Gold (Au)



Cadmium (Cd) versus Mercury (Hg)

'…cars start due to relativity' (relativity accounts for 85% of the voltage in a 2V lead–acid battery).
The Economist, 15 January, 2011
Original paper: *Ahuja, et.al, Phys. Rev. Lett., 106 (2011) 018301.*

Relativistic quantum mechanics Dirac equation (1928) :

$$\left(\beta mc^2 + c\,\boldsymbol{\alpha}\cdot\boldsymbol{\pi} + q\phi\right)\psi(r,t) = i\hbar\frac{\partial\psi(r,t)}{\partial t}$$

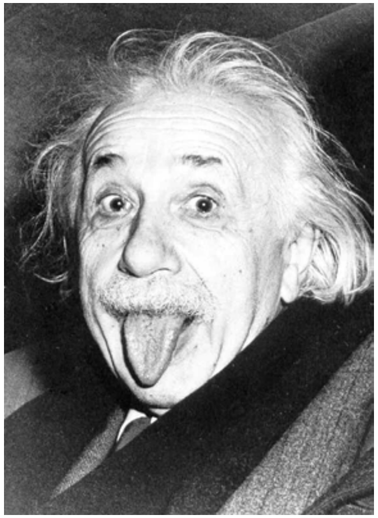
☺ First derivatives with respect to time and position
☺ Linear in scalar and vector potentials

☺ Can be shown to be Lorentz invariant

Alpha and Beta are <u>conventionally</u> represented by the following set of 4-component matrices

$$\alpha_x = \begin{pmatrix} 0 & \sigma_x \\ \sigma_x & 0 \end{pmatrix} \quad \alpha_y = \begin{pmatrix} 0 & \sigma_y \\ \sigma_y & 0 \end{pmatrix} \quad \alpha_z = \begin{pmatrix} 0 & \sigma_z \\ \sigma_z & 0 \end{pmatrix} \quad \beta = \begin{pmatrix} I & 0 \\ 0 & -I \end{pmatrix}$$

Influence of Relativity on Quantum World and vice-versa



$$\Psi(x) = \begin{pmatrix} \Psi_\alpha^L(\mathrm{x}) \\ \Psi_\beta^L(\mathrm{x}) \\ \Psi_\alpha^S(\mathrm{x}) \\ \Psi_\beta^S(\mathrm{x}) \end{pmatrix}$$

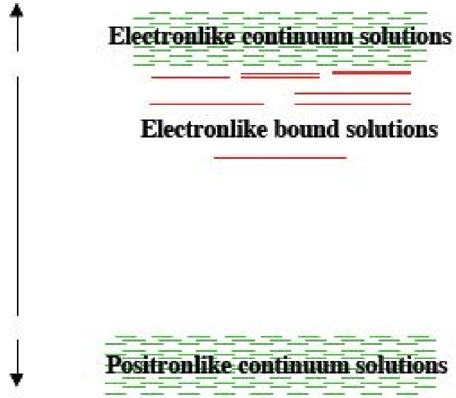
Four component wave function : why ?

1) Spin doubles the components

2) Negative energy solutions : $E < -mc^2$

The WORLD IS RELATIVISTIC AND THUS IS QUANTUM (and vice-versa!)

Dirac's sea of electrons. Quantum vacuum.



- All negative energy solutions are filled
- The Pauli principle forbids double occupancy
- ☺ Holes in the filled sea show up as particles with positive charge : positrons (discovered in 1933)
- ☹ Infinite background charge

The NR molecular wavefunction – physical meaning

- The wavefunction, Ψ, is a key quantity in quantum chemistry.
- Ψ depends on coordinates and spins. Spin of electron – relativistic property, additional “discrete” coordinate ; $|m_{s1}|=1/2$
- In a three dimensional system of *n*-electrons,

  $\left|\psi\left(x_1,\ldots,z_n,m_{s1},\ldots,m_{sn}\right)\right|^2 dx_1dy_1dz_1\ldots.dx_ndy_ndz_n$ is the probability of simultaneously finding electron 1 with spin m_{s1} in the volume $dx_1dy_1dz_1$ at (x_1,y_1,z_1), electron 2 with spin m_{s2} in the volume $dx_2dy_2dz_2$ at (x_2,y_2,z_2) and so on
- The wave function should be normalized, that is, the probability of finding all electrons somewhere in space equals 1.

$$\sum_{all\ m}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left|\psi\left(x_1,y_1,z_1,\ldots,x_n,y_n,z_n\right)\right|^2 dx_1dy_1dz_1\cdot\ldots\cdot dx_ndy_ndz_n=1$$

Wavefunction's general properties

- The wave function should be antisymmetric, that is, Ψ should change sign when two electrons of the molecule interchange:

$$\psi\left(x_1, y_1, z_1, \ldots, x_i, y_i, z_{i,\ldots,} x_j, y_j, z_j, \ldots, x_n, y_n, z_n, m_{s1}, \ldots, m_{sn}\right) =$$

$$-\psi\left(x_1, y_1, z_1, \ldots, x_j, y_j, z_j, \ldots, x_i, y_i, z_i, \ldots, x_n, y_n, z_n, m_{s1}, \ldots, m_{sn}\right)$$

- We can use the molecular wavefunction to calculate any property of the molecular system. The average value, $<C>$, of a physical property of our molecular system is:

$$\left\langle \hat{C} \right\rangle = \int \psi^* \hat{C} \psi \, d\tau \equiv \left\langle \psi \middle| \hat{C} \middle| \psi \right\rangle$$

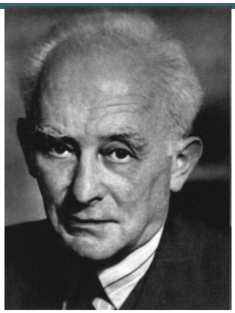
- where, $\hat{C}$, is the quantum mechanical operator of the physical property and
- $$\sum_{all\ m} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \ldots \int_{-\infty}^{\infty} dx_1 dy_1 dz_1 \cdot \ldots \cdot dx_n dy_n dz_n = \int d\tau$$

Ab-initio Wavefunction approach

Ab-initio Wavefunction approach

- Simplifying assumptions are employed to 'solve' the Schrödinger equation approximately:
  - **<u>Born-Oppenheimer approximation</u> allows separate treatment of nuclei and electrons**
  - **<u>Hartree-Fock independent electron approximation</u> allows each electron to be considered as being affected by the sum (field) of all other electrons.**
  - **<u>MOLCAO Approximation</u>**
- Tools: Variational Principle or Perturbation Theory

Born-Oppenheimer Approximation

 - 

$$\hat{H} = -\frac{h^2}{8\pi^2}\sum_{A}^{\text{nuclei}}\frac{1}{M_A}\nabla_A^2 - \frac{h^2}{8\pi^2 m}\sum_{a}^{\text{electrons}}\nabla_a^2 - e^2\sum_{A}^{\text{nuclei}}\sum_{a}^{\text{electrons}}\frac{Z_A}{r_{Aa}}$$

kinetic energy (nuc.) kinetic energy (elect.)

$$+ e^2\sum_{A>B}^{\text{nuclei}}\frac{Z_A Z_B}{r_{AB}} + e^2\sum_{a>b}^{\text{electrons}}\frac{1}{r_{ab}}$$

constant

1 kinetic energy term plus
2 Coulombic energy terms:
(one attractive, 1 repulsive)
plus a constant for nuclei

Steps of solution of the Schrödinger equation in the Born-Oppenheimer approximation:

$$H_{tot} = (T_n + V_n) + T_e + V_{ne} + V_e = (H_n) + H_e$$

1. **Electronic SE:** $H_e \Psi_e(r,R) = E_e(R)\, \Psi_e(r,R)$
2. **Nuclear SE:** $(T_n + V_n + E_e(R))\Omega_n(R) = E_n\, \Omega_n(R)$

   $V_n + E_e(R)$ **= potential energy surface (PES)**

TOTAL WF : $\Phi(r,R) = \Omega_n(R)\, \Psi_e(r,R)$

In our laboratory we concentrate mainly on solution of the electronic SE and working with PES (finding minimums, transition states etc.)

Solving the Electronic SE: Hartree-Fock (HF) approximation – the physical background

- **Multi-electronic SE:** $H_e \Psi_e (r,R) = E_e(R) \Psi_e (r,R)$ **is still very complicated $\rightarrow$ reduce it to the single-electronic equation**
- **HF assumes that each electron experiences all the others only as a whole (field of charge) rather than individual electron-electron interactions.**
- **Instead of multielectronic Shrödinger equation introduces a one-electronic Fock operator *F*:**

$$F \phi = \varepsilon \phi$$

which is the sum of the kinetic energy of an electron, a potential that one electron would experience for a fixed nucleus, and an <u>average of the effects of the other electrons</u>.

Mathematical foundation of the HF (or Self-consistent-field (SCF)) method

- **Molecular orbital theory approximates the molecular wave function Ψ as a antisymmetrized product of orthonormal one-electron functions (or "molecular spin-orbitals")**
- $$\psi = \hat{A}(f_1 \times f_2 \times \dots \times f_n)$$
- **where Â is the antisymmetrization operator and** $f_i = \phi_i(x_i, y_i, z_i)\sigma_k$
- **where** $k = \pm 1/2$; $\sigma_{1/2} = \alpha$; $\sigma_{-1/2} = \beta$.
- **The antisymmetrization operator is defined as the operator that antisymmetrizes a product of n one-electron functions and multiplies them by normalization factor** $(n!)^{-1/2}$

Determinant of Slater

- The antisymmetrized WF can be represented as the Slater's determinant:

$$\Psi = \left(n!\right)^{-1/2} \begin{vmatrix} \phi_1(x_1)\alpha(1) & \phi_1(x_1)\beta(1) & \phi_2(x_1)\alpha(1) & \phi_2(x_1)\beta(1) & \dots & \phi_{n/2}(x_1)\beta(1) \\ \phi_1(x_2)\alpha(2) & \phi_1(x_2)\beta(2) & \phi_2(x_2)\alpha(2) & \phi_2(x_2)\beta(2) & \dots & \phi_{n/2}(x_2)\beta(2) \\ \dots & & & & & \dots \\ \phi_1(x_n)\alpha(n) & \phi_1(x_n)\beta(n) & \phi_2(x_n)\alpha(n) & \phi_2(x_n)\beta(n) & \dots & \phi_{n/2}(x_n)\beta(n) \end{vmatrix}$$

Variational Principle

- **The energy *E* calculated from <u>any</u> approximation of the wavefunction *Φ* will be <u>higher</u> than the true energy E_0:**

$$E = \int \Phi^* \hat{H} \Phi d\tau \geq E_0$$

- **The better the wavefunction, the lower the energy (the more closely it approximates reality).**
- **Changes (variation of parameters in *Φ*) are made systematically to minimize the calculated energy.**
- **At the energy minimum (which approximates the true energy of the system) for HF : $\partial E/\partial \varphi_i = 0$.**

The Hartree-Fock energy functional

- We shall restrict ourselves to closed shell configurations, for such cases, a single Slater determinant is sufficient to describe the molecular wave function. Using the variational principle within this framework lead to the restricted HF theory. The Hartree-Fock energy for molecules with only closed shells is

$$E_{HF} = 2\sum_{i=1}^{n/2} H_i^{core} + \frac{1}{2}\sum_{i=1}^{n/2}\sum_{j=1}^{n/2}(2J_{ij} - K_{ij})$$

$$H_i^{core} \equiv \left\langle \phi_i(1) \middle| \hat{H}^{core}(1) \middle| \phi_i(1) \right\rangle = \left\langle \phi_i(1) \middle| -\frac{1}{2}\nabla_1^2 - \sum_I Z_I / r_{1I} \middle| \phi_i(1) \right\rangle$$

$$J_{ij} \equiv \left\langle \phi_i(1)\phi_j(2) \middle| 1/r_{12} \middle| \phi_i(1)\phi_j(2) \right\rangle, \quad K_{ij} \equiv \left\langle \phi_i(1)\phi_j(2) \middle| 1/r_{12} \middle| \phi_j(1)\phi_i(2) \right\rangle$$

The Hartree-Fock equations

- The Hartree-Fock equations are derived from the variational principle, which looks for those orbitals φ that minimize E_{HF}.
- For computational convenience the molecular orbitals are taken to be orthonormal: $\langle \phi_i(1) | \phi_j(1) \rangle = \delta_{ij}$
- The orthogonal Hartree-Fock molecular orbitals satisfy the single-electronic equations:

$$\hat{F}(1)\phi_i(1) = \varepsilon_i \phi_i(1)$$

The *(Hartree-) Fock operator*

- Single-electronic operator:

$$\hat{F}(1) = \left| -\frac{1}{2}\nabla_1^2 - \sum_I Z_I / r_{1I} \right| + \sum_{j=1}^{n/2} \left[2\hat{J}_j(1) - \hat{K}_j(1) \right]$$

- The ***Coulomb operator*** $\boldsymbol{J_j}$ and the ***exchange operator*** $\boldsymbol{K_j}$ are defined by

$$\hat{J}_j(1) f(1) = f(1) \int \left| \phi_j(2) \right|^2 \frac{1}{r_{12}} dv_2$$

$$\hat{K}_j(1) f(1) = \phi_j(1) \int \frac{\phi_j^*(2) f(2)}{r_{12}} dv_2$$

- where f is an arbitrary function

Next step: MO-LCAO Approximation

- **Electron positions in molecular orbitals can be approximated by a Linear Combination of Atomic Orbitals (LCAO).**
- **This reduces the problem of finding the best functional form for the molecular orbitals to the much simpler one of optimizing a set of coefficients (c_n) in a linear equation:**

$$\phi = c_1 \chi_1 + c_2 \chi_2 + c_3 \chi_3 + c_4 \chi_4 + \ldots$$

where ϕ is the molecular orbital (MO) wavefunction and χ_n represent atomic orbital (AO) wavefunctions.

One step more: Basis sets (BS)

- **A basis set is a set of analytical functions (ξ_k) used to represent the shapes of atomic orbitals χ_n:**
- **General contracted BS: $\chi_n = \Sigma_k b_{k(n)} \xi_{k(n)}$**
- **Contraction coefficients are calculated in a separate atomic HF calculation;**
  if k=1 basis set is called uncontracted.
- **Basis sets in common use have a simple mathematical form for representing the radial distribution of electron density.**
- **Most commonly used are Gaussian-Type orbitals (GTO), which approximate the better, but more numerically complicated Slater-Type orbitals (STO).**

Hartree-Fock Self-Consistent Field (SCF) Method.

Computational methodology (Jacobi iterations):

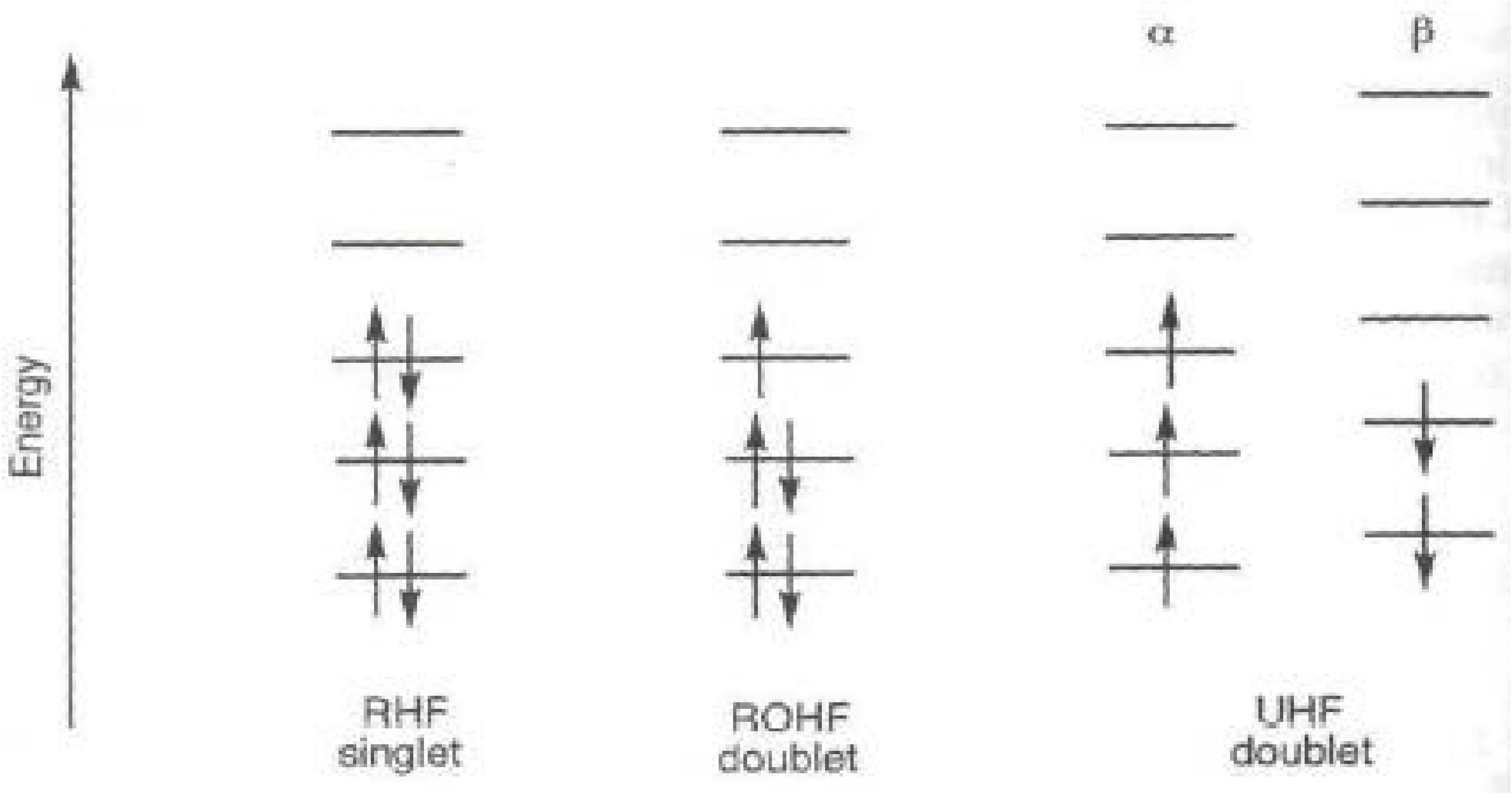
1. **Guess the orbital occupation (position) of an electron (set of MO coefficients $\{c_n\}$)**
2. **Calculate the potential each electron would experience from all other electrons (Fock operator $F(\{c_n\})$)**
3. **Solve for Fock equations to generate a new, improved guess at the positions of the electrons (new $\{c_n\}$)**
4. **Repeat above two steps until the wavefunction for the electrons is consistent with the field that it and the other electrons produce (SCF).**

Types of HF

- **Multiplicity (*M*) = $2*S+1$**
  (*S* is the total spin of the system)
- Electrons can have spin up or down . **Most calculations are closed shell calculations ($M=1$), using doubly occupied orbitals, holding two electrons of opposite spins. RHF – restricted HF**
- **Open shell systems ($M>1$) are calculated by**

1. **ROHF – restricted open shell HF – the same spatial orbitals for different spin-orbitals from the valence pair;**
2. **UHF – unrestricted HF – different spatial parts for different spins from the same valence pair**

Illustrating an RHF singlet, and ROHF and UHF doublet states



Semi-empirical MO Calculations: Further Simplifications of HF

$$H_{ii}^{core} \equiv \left\langle \phi_i(1) \middle| \hat{H}^{core}(1) \middle| \phi_i(1) \right\rangle = \left\langle \phi_i(1) \middle| -\frac{1}{2}\nabla_1^2 - \sum_I Z_I / r_{1I} \middle| \phi_i(1) \right\rangle$$

$$J_{ij} \equiv \left\langle \phi_i(1)\phi_j(2) \middle| 1/r_{12} \middle| \phi_i(1)\phi_j(2) \right\rangle, \quad K_{ij} \equiv \left\langle \phi_i(1)\phi_j(2) \middle| 1/r_{12} \middle| \phi_j(1)\phi_i(2) \right\rangle; \quad \phi_i = \sum_{A,\mu} c_{i\mu A}\chi_\mu^A$$

$$\langle \mu | \nu \rangle = \int (\chi_\mu^A(1))^* \widehat{H}^{core}(1)\chi_\lambda^C(1)d\tau_1; \ \langle \mu\nu | \lambda\sigma \rangle = \iint (\chi_\mu^A(1))^* (\chi_\lambda^C(2))^* \frac{1}{r_{12}} \chi_\nu^B(1)\chi_\sigma^D(2)d\tau_1 d\tau_2$$

- **Neglect core (1s) electrons; replace integral for H_{core} by an empirical or calculated parameter**
- **Neglect various other interactions between electrons on adjacent atoms: CNDO:** $\langle \mu\nu | \lambda\sigma \rangle = \delta_{\mu\lambda}\delta_{\nu\sigma}\langle \mu\nu | \mu\nu \rangle$ **, INDO, MINDO, PM3,AM1, etc.(iterative); Huckel – non-iterative**
- **Add parameters so as to make the simplified calculation give results in agreement with observables (atomic spectra or molecular properties).**

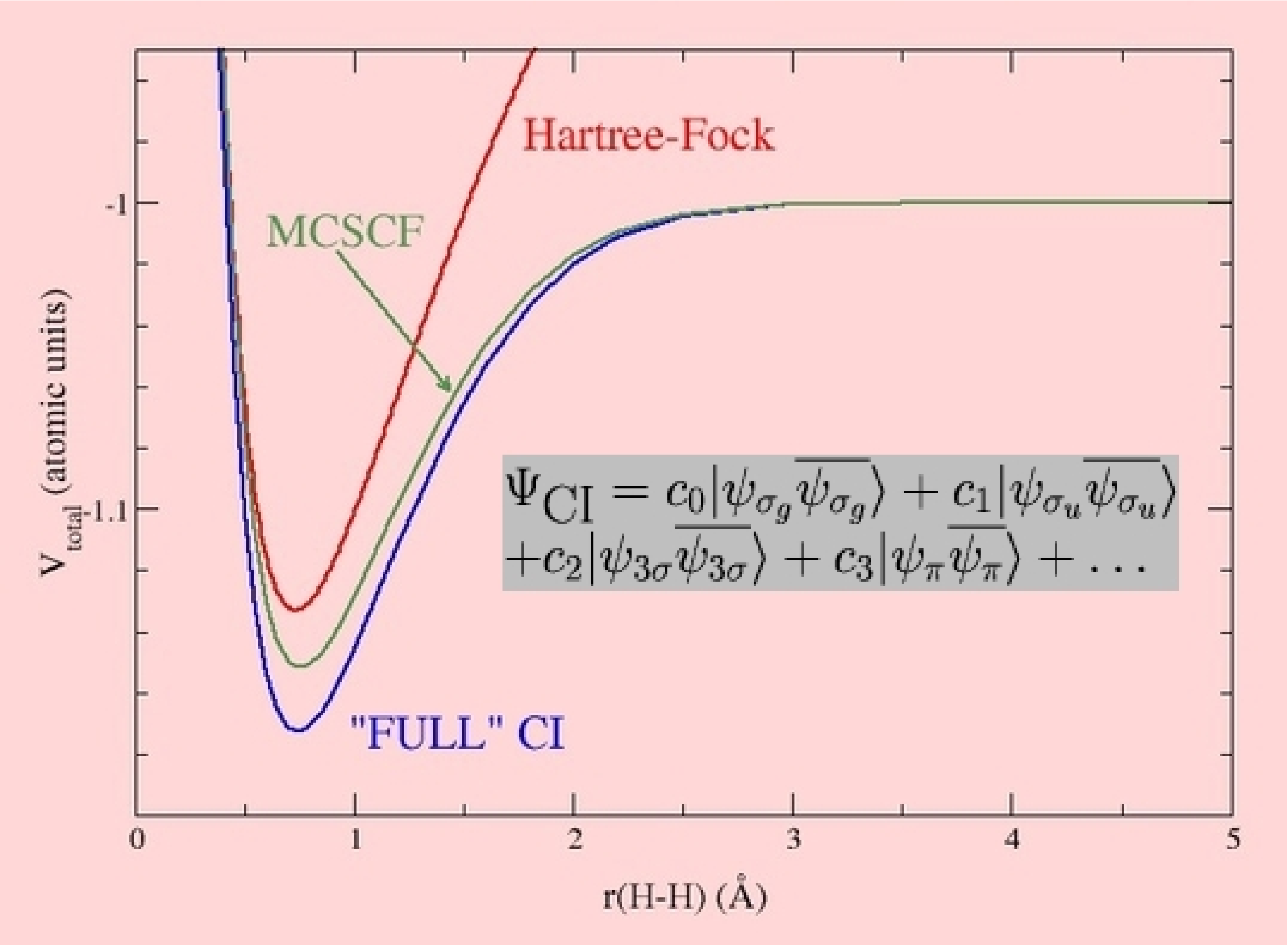
Beyond the SCF. Correlated Methods (CM)

- Include more explicit interaction of electrons than HF :

$E_{corr} = E - E_{HF}$, where $E\Psi = H\Psi$

- Most CMs begin with HF wavefunction, then incorporate varying amounts of electron-electron interaction by mixing in excited state determinants with ground state HF determinant
- The limit of infinite basis set & complete electron correlation is the exact solution of Schrödinger equation (which is still an approximation)

Beyond the SCF.
Correlation effects on properties.



Two alternative ways of the electron correlation treatment

HF (Hartree-Fock) – "a singe determinant" theory

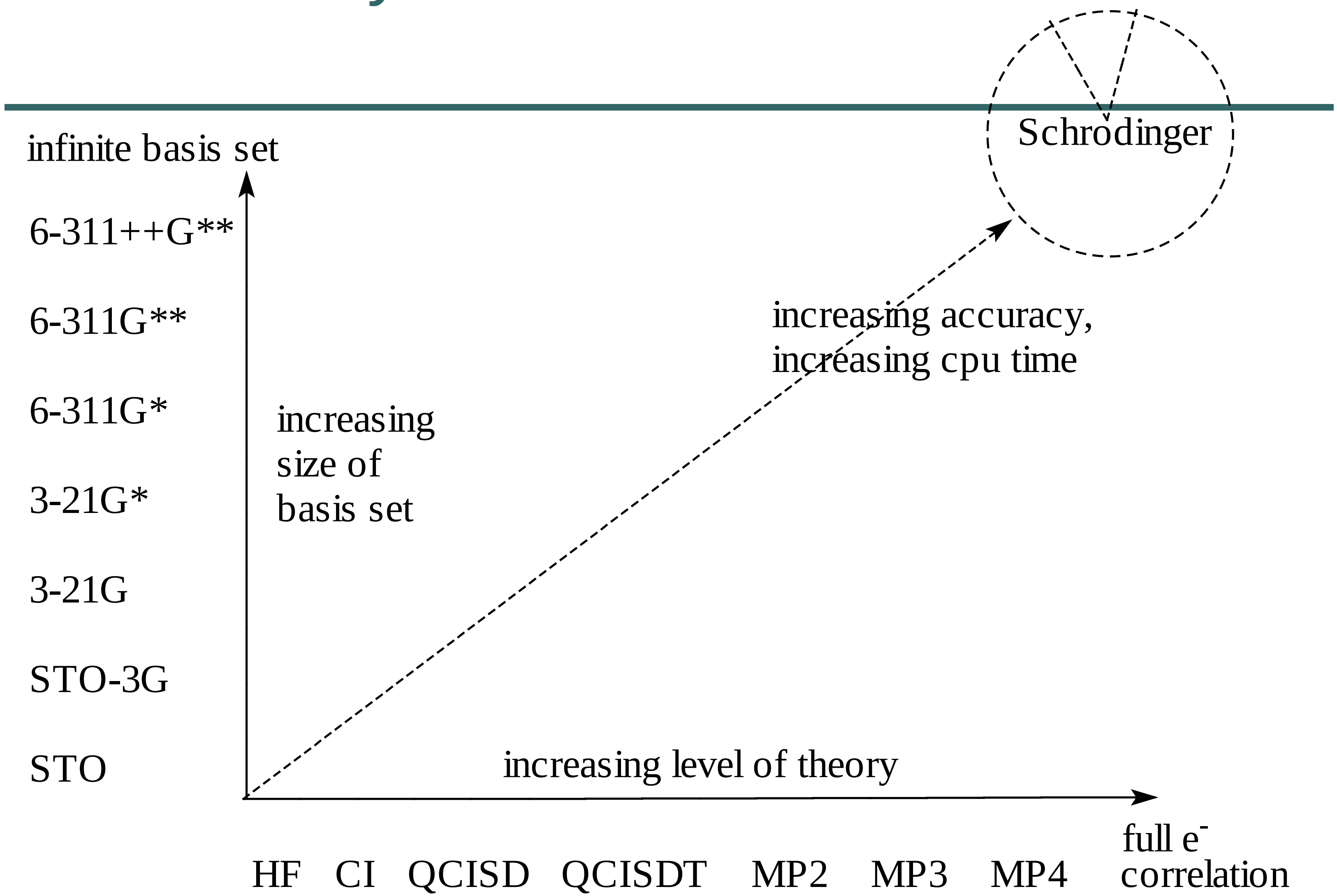
- **no correlation included!**

1. **WF based "multi-determinant" correlation methods:**
   1. **<u>Configuration Interaction</u> (CI) (+ <u>statistical Monte-Carlo (MC)</u>)**
      - ***Variational*: CISD, CSID(T) … *Non-variational*: DMRG, DMC**
   2. **<u>Many-body perturbation theory</u> (including *infinite-orders* methods)**
      - ***Non-variational (+ variatioanal)* MBPT2, MBPT3; CCSD; CCSD(T)**
2. **Density functional theory (DFT) – correlation method not based on wave-function, but rather on modification of the energy functional:**

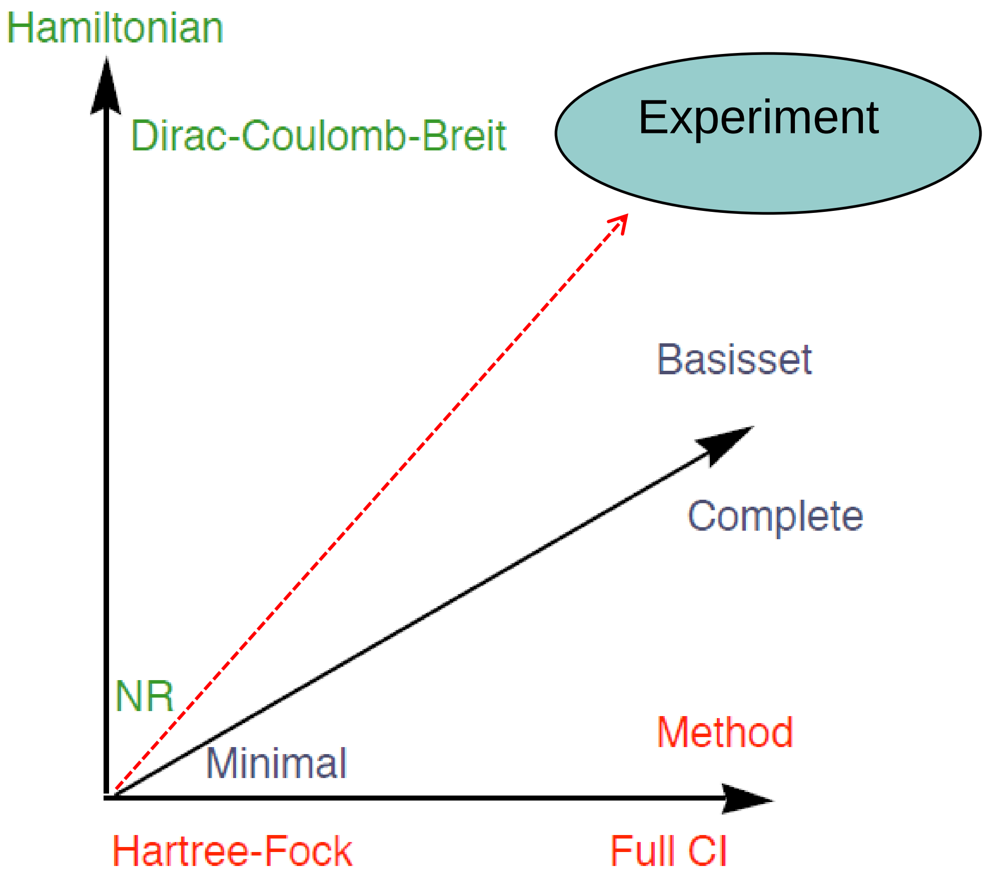
$$E_{DFT} = 2\sum_{i=1}^{n/2} H_i^{core} + \sum_{i=1}^{n/2}\sum_{j=1}^{n/2}(J_{ij} + X^{Exch+Corr}{}_{ij})$$

Kohn-Sham: A "single determinant" theory including correlation!

Summary of Choices:



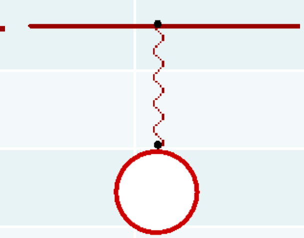
The extra dimension:



Hierarchy of effects: IP of Au - breaking the meV precision

(L. Pasteka, E.E., A.Borschevsky, and P. Shwerdtfeger; *PRL 118, 023002 (2017)*)

Contribution	eV							
SCF	NR	REL						
	5.9864	1.7028						
Correlation	CCSD	d(T)	dT	d(Q)	dQ	d(P)	dP	total
All electron	1.4271	0.1774						
valence (5d6s)			-0.0221	0.0048	0.0010	-0.0014	0.0009	-0.0167
core (4f5s5p)			-0.0074	0.0005	0.0000	0.0000	0.0000	-0.0070
sum			-0.0295	0.0053	0.0010	-0.0014	0.0009	**-0.0237**
Breit	Ω=0; (SCF)	Ω; (SCF)	Ω=0; (CC)	total	$B_{12} = -\frac{1}{2r_{12}}\left[\vec{\alpha}_1 \bullet \vec{\alpha}_2 + (\vec{\alpha}_1 \bullet \vec{r}_{12})(\vec{\alpha}_2 \bullet \vec{r}_{12})/r_{12}^2\right]$			
	-0.0127	-0.0005	-0.0024	**-0.0156**				
QED	PT(1)	SCF	CCSD	total		SE		VP
SE	-0.0264	0.0003	-0.0058	-0.0319				
VP	0.0053	-0.0004	0.0012	0.0061				
sum	-0.0211	0.0003	-0.0046	**-0.0258**				
Final IP	**Theory**	**Experim.**	**Difference**					
	9.2286	**9.2256**	**0.0030**					

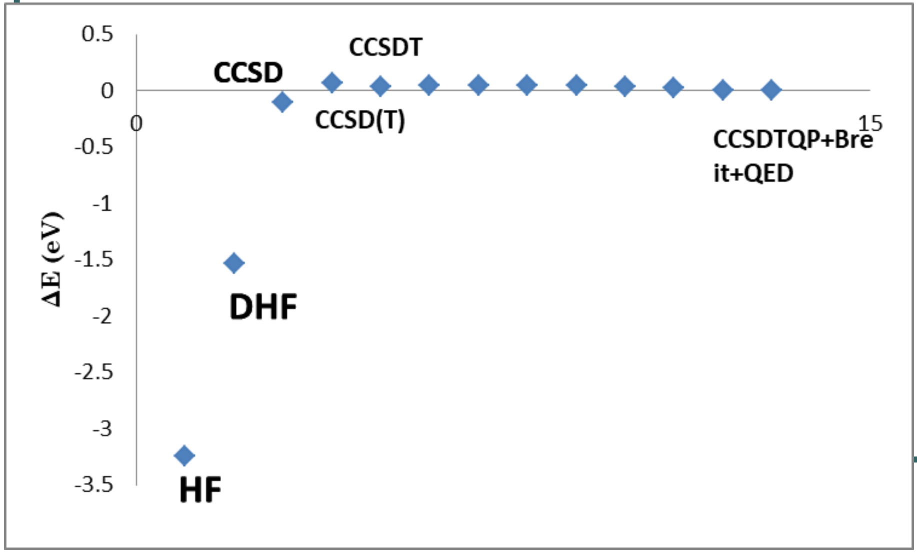


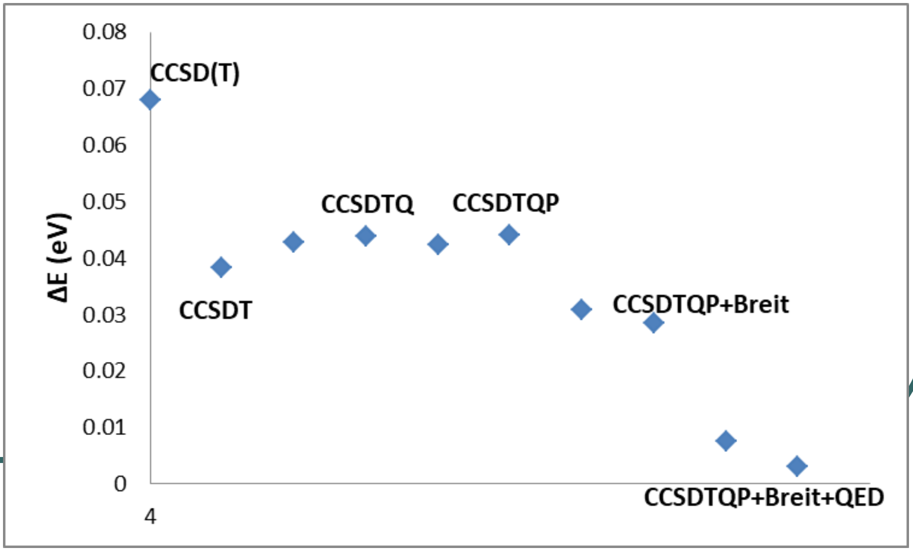
Reaching meV accuracy: IP and EA of gold

Final results

	IP (eV)	ΔE (eV)	EA (eV)	ΔE (eV)
4c-CCSDTQP+Breit+QED	**9.2288**	**0.0030**	**2.3072**	**0.0014**

IP (exp.)=9.2256 eV, EA (exp.)=2.3086 eV



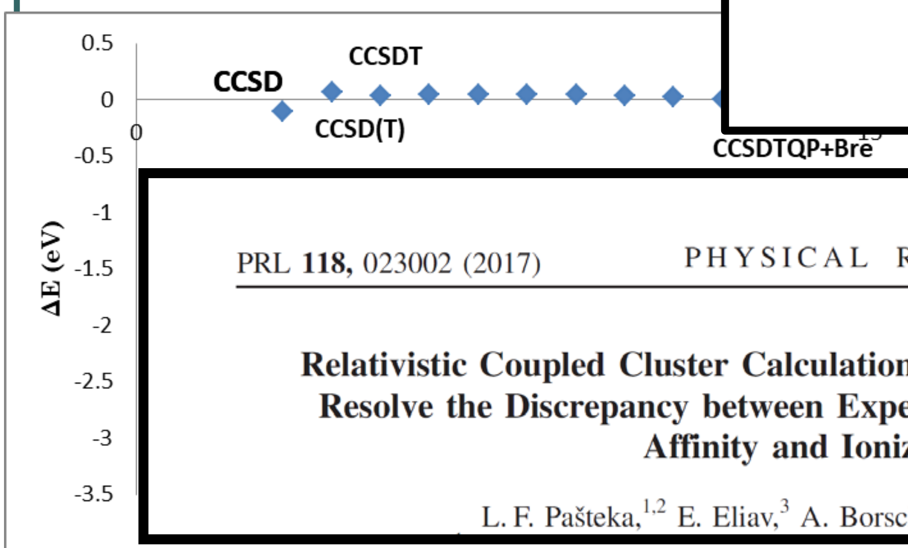


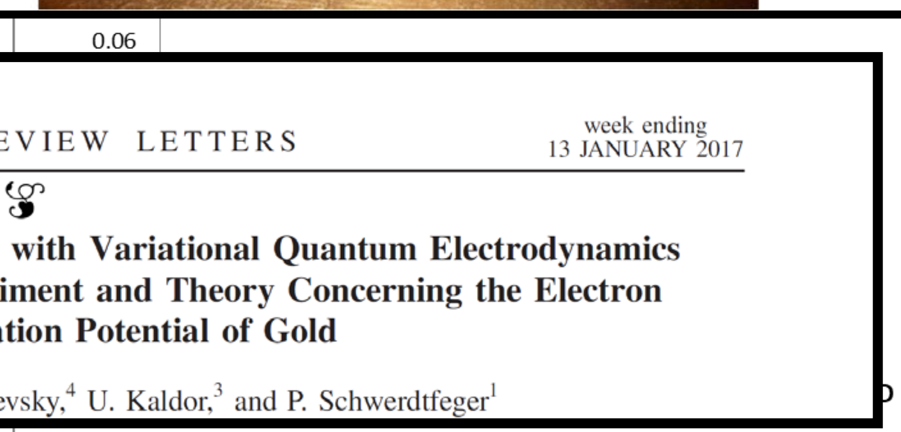
Reaching meV accuracy: IP and EA of gold

Final results

4c-CCSDTQP+Breit+QED	

IP (exp.)=9.2256 eV, E





Synopsis: Golden Mystery Solved

January 10, 2017

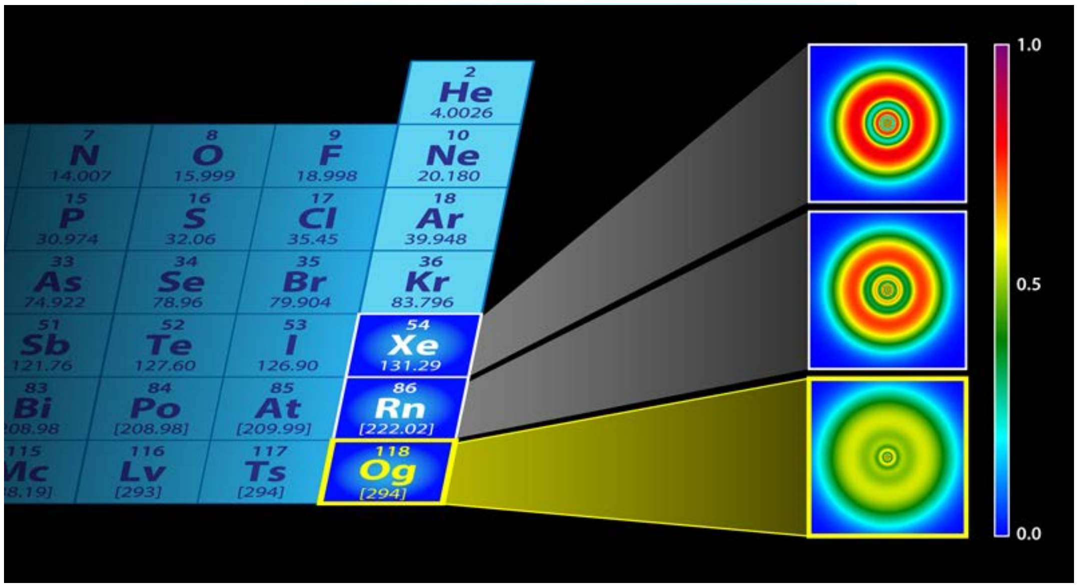
A long-standing discrepancy between experiments and theory concerning the electronic properties of gold has now been resolved.

PRL **118,** 023002 (2017) PHYSICAL REVIEW LETTERS week ending 13 JANUARY 2017

Relativistic Coupled Cluster Calculations with Variational Quantum Electrodynamics Resolve the Discrepancy between Experiment and Theory Concerning the Electron Affinity and Ionization Potential of Gold

L. F. Pašteka,[1,2] E. Eliav,[3] A. Borschevsky,[4] U. Kaldor,[3] and P. Schwerdtfeger[1]

Even more relativity & correlation: SHEs
Oganesson (E118) – the first active Inert Gas



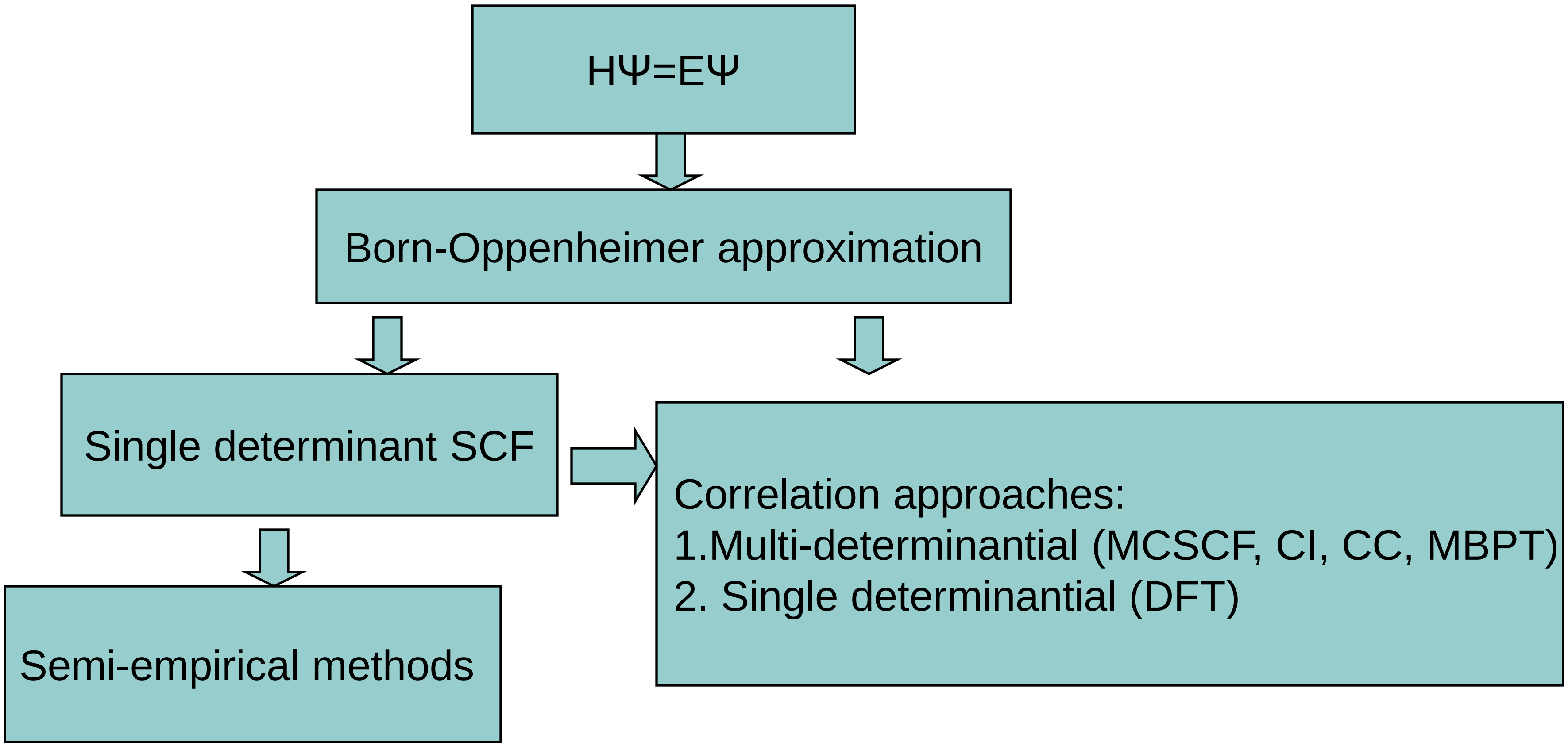
Theoretical calculations of the electronic structure of Og show that the distribution of electrons is smooth, as one would expect for a gas of noninteracting particles. This uniform behavior contrasts with the shell structure observed in lighter elements like xenon (Xe) and radon (Rn), shown in the top and middle panels. [Credit: P. Jerabek *et al.* Phys. Rev. Lett. 120, 053001 (2018).]

A tiny interplay between relativity and electron correlation. Nonrelativistic or uncorrelated calculations give no electron affinity for the element E118 - Oganesson.

QED contribution large (about 10%)

(EE, et al, PRA, 67, 020102 (2003))

Summary: Levels of *QM* Theory



Some applications during your work...

- **Calculation of reaction pathways (mechanisms)**
- **Determination of reaction intermediates and transition structures**
- **Visualization of orbital interactions (formation of new bonds, breaking bonds as a reaction proceeds)**
- **Shapes of molecules including their charge distribution (electron density)**
- **NMR chemical shift prediction.**
- **IR spectra calculation and interpretation.**

Method Type	**Features**	**Advantages**	**Disadvantages**	**Best for**
Molecular Mechanic	Uses classical physics • Relies on force-field with embedded empirical parameters • Computationally least intensive - fast and useful with limited computer resources	Good for: • Enthalpy of Formation (sometimes) • Dipole Moment • Geometry (bond lengths, bond angles, dihedral angles) of lowest energy conformation.	Particular force field, applicable only for a limited class of molecules • Does not calculate electronic properties • Requires experimental data (or data from *ab initio* calculations)	Large systems (~1000 of atoms) • Can be used for molecules as large as enzymes • Systems or processes with no breaking or forming of bonds
Semi-Empirical	Uses quantum physics • Uses experimentally derived empirical parameters • Uses many approximations	Less demanding computationally than *ab initio* methods • Capable of calculating transition states and excited states	Requires experimental data (or data from *ab initio*) for parameters • Less rigorous than *ab initio*) methods	Medium-sized systems (hundreds of atoms) • Systems involving electronic transition
Ab Initio	Uses quantum physics • Mathematically rigorous, no empirical parameters • Uses approximation extensively	Useful for a broad range of systems • does not depend on experimental data • Capable of calculating transition states and excited states	Computationally expensive	Small systems (tens of atoms) • Systems involving electronic transition • Molecules without available experimental data • Systems requiring rigorous accuracy