Ab-initio quantum chemistry – a road map

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A small document motivating our daily struggle with quantum mechanics for chemistry.

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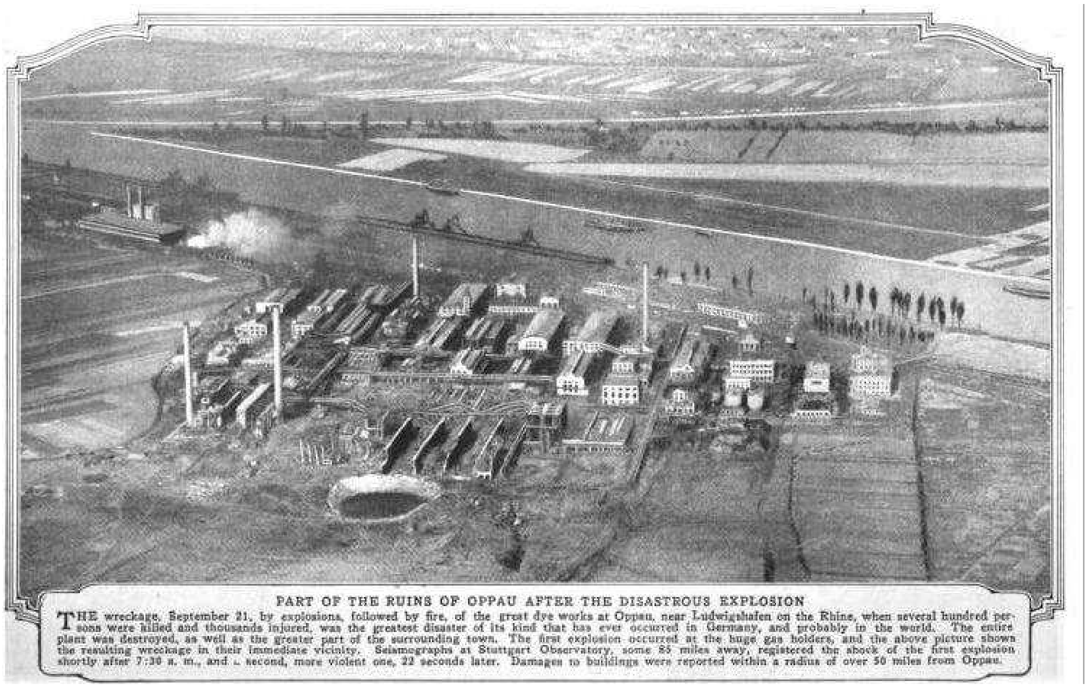
I. WHY THEORETICAL (QUANTUM) CHEMISTRY

- not toxic
- not explosive



PART OF THE RUINS OF OPPAU AFTER THE DISASTROUS EXPLOSION

THE wreckage, September 21, by explosions, followed by fire, of the great dye works at Oppau, near Ludwigshafen on the Rhine, when several hundred persons were killed and thousands injured, was the greatest disaster of its kind that has ever occurred in Germany, and probably in the world. The entire plant was destroyed, as well as the greater part of the surrounding town. The first explosion occurred at the huge gas holders, and the above picture shows the resulting wreckage in their immediate vicinity. Seismographs at Stuttgart Observatory, some 85 miles away, registered the shock of the first explosion shortly after 7:30 a. m., and a second, more violent one, 22 seconds later. Damages to buildings were reported within a radius of over 50 miles from Oppau.

FIG. 1. Explosion in Oppau 1921, 4500 tons NH_4NO_3 and $(NH_4)_2SO_4$, $\approx$ 600 victims. Illustration from Popular Mechanics Magazine 1921

- few fundamental laws

II. WHAT TO DO ?

Solve Schrödinger's equation

$$\hat{H}\,\Psi \;=\; E\,\Psi \tag{1}$$

E. Schrödinger “An undulatory theory of the mechanics of atoms and molecules”, Phys.Rev. **28** (1926) 1049

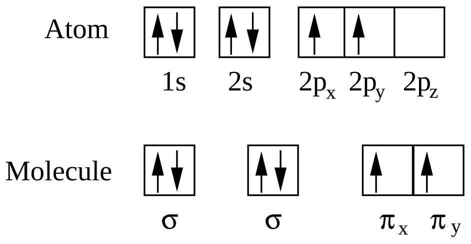
”The general theory of quantum mechanics is now complete... The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known.”

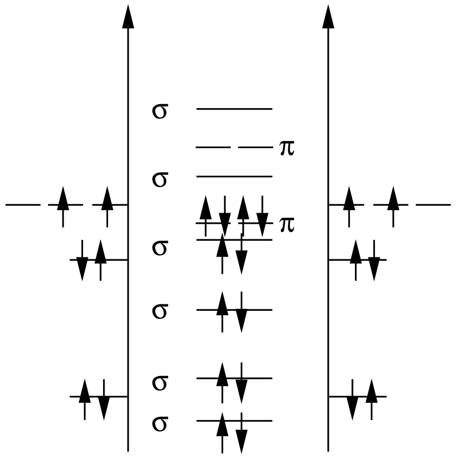
P.A.M. Dirac “Quantum Mechanics of Many-Electron Systems”, Proc.R.Soc.Lond. **A123** (1929) 714-733

III. HOW TO START

Write down $\hat{H}$ and a form of Ψ.

Too complicated ? Start simpler.





- Where do they come from ?
- Are they always valid ?
- How to achieve chemical accuracy ?

IV. SIMPLEST MULTI-ELECTRON WAVEFUNCTION RESPECTING PAULI’S PRINCIPLE

Slater determinant, built from occupied orbitals

$$\Psi(\vec{r}_1,\sigma_1,\vec{r}_2,\sigma_2,\ldots,\vec{r}_2,\sigma_n) \;=\; \frac{1}{\sqrt{n!}}\begin{vmatrix} \phi_1(\vec{r}_1)\sigma_1 & \phi_1(\vec{r}_2)\sigma_1 & \ldots & \phi_1(\vec{r}_n)\sigma_1 \\ \phi_2(\vec{r}_1)\sigma_2 & \phi_2(\vec{r}_2)\sigma_2 & \ldots & \phi_2(\vec{r}_n)\sigma_2 \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(\vec{r}_1)\sigma_n & \phi_n(\vec{r}_2)\sigma_n & \ldots & \phi_n(\vec{r}_n)\sigma_n \end{vmatrix} \tag{2}$$

for fixed positions of the nuclei (Born-Oppenheimer approximation, justified by the mass difference of electrons and protons).

V. TOTAL ENERGY

$$E \;=\; \langle\Psi|\hat{H}|\Psi\rangle \;\;\text{but not}\;\; \hat{H}\,\Psi \;=\; E\,\Psi \tag{3}$$

Best orbitals: minimize $\langle\Psi|\hat{H}|\Psi\rangle$ with respect to orbital parameters. The Hamiltonian $\hat{H}$ contains

- the kinetic energy $-(1/2)\Delta$ of each electron
- the electron-nucleus attraction
- the electron-electron repulsion
- perhaps external fields, acting on each electron individually

This approach is called the **Hartree-Fock approximation**, one single determinant and the exact non-relativistic Hamiltonian. We do not solve Schrödinger's equations, but we use the variational principle: the total energy $\langle\Psi|\hat{H}|\Psi\rangle$ is always higher than the energy for the exact solution of Schrödinger's equation. So we do the best we can with one single determinant.

VI. HOW DOES HARTREE-FOCK PERFORM

- Good geometries, slightly too short bond lengths
- Good ionization potentials (Koopmans theorem)
- Bad binding energies (50 % of experimental values)
- Bad vibrational frequencies (much too high)
- Incapable to dissociate closed-shell systems continously into two separated open-shell systems
- Only high-spin states possible, no open-shell singlet for instance

VII. WHAT PROPERTIES CAN WE CALCULATE

- Total energy ⟶ geometry optimization, dissociation energies (but no continuous dissociation potential curves, only the difference between equilibrium and end points), formation enthalpies, vibrational spectra, rotational constants, polarizabilities
- Orbitals ⟶ density, multipolar moments, population analysis, atomic basins
- Orbital energies ⟶ excitation energies, ionization potentials, electron affinities

VIII. HOW CAN WE GO BEYOND THE HARTREE-FOCK APPROXIMATION

- Change the total energy expression by adding a density-dependent exchange-correlation term $E_{XC}[\rho]$, but keep the single-determinant wavefunction and the variational principle: **DFT**. As the functional is not exactly known, the variational principle does not lead to the correct Schrödinger equation. Justification of DFT: the electronic density gives through Kato's theorem (locally $(\nabla\rho)/\rho = 2\,Z$) the positions and Z of the nuclei, thus one can write the exact Schrödinger equation to be solved — from the knowledge of the eletronic density only.
- Take into account experimental results for creating parametrized model hamiltonians and find energy minima through variation of orbital parameters: **semi-empirical methods**. Again, the variational principle does not guarantee the exact energy.
- Go to multi-determinantal wavefunctions:
  - no single set of occupied orbitals any more for the system
  - binding energies, total energy: electron correlation needed, **dynamical correlation**
  - bond breaking, open-shell singlets : several determinants of comparable weight, **non-dynamical correlation**

IX. TREATING DYNAMICAL CORRELATION

Definition of the (dynamical) correlation energy:

$$E_{\mathrm{Corr}} \;=\; E_{total} - E_{HF} \tag{4}$$

A. By perturbation

Cut Hamiltonian in two parts and Ψ and E in power series

$$\hat{H}(\lambda) = \hat{H}_0 + \lambda\,\hat{V} \quad ; \qquad \Psi(\lambda) = \sum_{k=0}^{\infty} \lambda^k \Psi^{(k)} \quad ; \qquad E(\lambda) = \sum_{k=0}^{\infty} \lambda^k E^{(k)} \tag{5}$$

Write down $\hat{H}(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda)$, and sort by common orders in λ. Leads to order-by-order contributions to the total energy and the wavefunction. Energies:

$$E_0^{(n)} \;=\; \langle\, 0\,|\,\hat{V}\,|\,n-1\,\rangle \tag{6}$$

Coefficients:

$$\begin{aligned} c_k^{(n)} \;=\; \langle\Phi_k|\Psi^{(n)}\rangle \;=\; & \frac{1}{E_0^{(0)} \;-\; E_k^{(0)}}\Big[\langle\, k\,|\,\hat{V}\,|\,n-1\,\rangle \\ & -E_0^{(1)}\,c_k^{(n-1)} \;-\; E_0^{(2)}\,c_k^{(n-2)} - \ldots - E_0^{(n-1)}c_k^{(1)}\Big] \end{aligned} \tag{7}$$

- No explicit wavefunction, density, orbitals and orbital energies
- The first-order wavefunction is assumed to be a good approximation for the exact wavefunction
- Method is size-consistent in any order
- Each order adds a factor of the number of basis functions for the computational cost: MP2$\sim$N^5, MP3$\sim$N^6, MP4$\sim$N^7 etc.
- First-order energy is always the Hartree-Fock energy, independent of the decomposition into $\hat{H}_0$ and $\hat{V}$.
- Only the infinite order satisfies Schrödinger's equation $\hat{H}\Psi \ = \ E \ \Psi$.
- Wigner's $2n+1$ rule : from the coefficients in order n we may calculate the energy in order $2n+1$: For instance from the 1st-order coefficients we obtain the energy in 3rd order.
- Formulas give energies which are not invariant to orbital rotations, like localizations.

B. By variation

$$\Psi \ = \ \Phi_{HF} + \sum_{ia} c_i^a \, \Phi_i^a + \sum_{ijab} c_{ij}^{ab} \, \Phi_{ij}^{ab} + \ldots \tag{8}$$

Minimizing $\langle\Psi|\hat{H}|\Psi\rangle$ with respect to the c_i^a, c_{ij}^{ab} leads to a system of **linear** equations, equivalent to finding the lowest eigenvalue of the hamilton matrix in the determinantal basis, i.e. the matrix of the elements $\langle\Phi_I|\hat{H}|\Phi_J\rangle$. The correlation energy is determined via the coefficients of the double excitations:

$$E_{\text{Corr}} \ = \ \sum_{ijab} c_{ij}^{ab} \langle\Phi_{HF}|\hat{H}|\Phi_{ij}^{ab}\rangle \tag{9}$$

The method is called "Configuration Interaction" (CI).

- Explicit wavefunction and density. No orbitals and orbital energies.
- Full CI (i.e. all possible configurations) grows exponentially with the size of the basis
- Limited expansion schemes (e.g. CISD with single and double excitations only) are NOT size-consistent. Corrections possible (Davidson correction, CEPA, ACPF, AQCC, (SC)^{2}CI).
- As only c_{ij}^{ab} enter the correlation energy, one may argue that this part of the wavefunction represents better the wavefunction than the simple CISD.
- From the variational principle follows that the energy is independent of orbital rotations.

C. Selection schemes combining perturbation and variation

Calculate pertubational contribution of each doubly excited determinant to the correlation energy. Select the most important ones, and add all single- and double excited determinants of the selected ones to the wavefunction. Minimize the total energy variationally. Extrapolate for vanishing selection criterion. CIPSI (J.P. Malrieu, Toulouse) or MRDCI (S. Peyerimhoff, R. Bunker, Bonn).

D. The Coupled-Cluster approach

$$\Psi \;=\; e^{\hat{S}}\,\Phi_{HF} = \left(1 + \hat{S} + \frac{1}{2}(\hat{S})^2 + \frac{1}{3!}(\hat{S})^3 + \ldots\right)\,\Phi_{HF} \tag{10}$$

with the excitation operator $\hat{S} = \sum_{ia} t_i^a \hat{a}_a \hat{a}_i^\dagger + \sum_{ijab} t_i^a \hat{a}_a \hat{a}_b \hat{a}_i^\dagger \hat{a}_j^\dagger \;=\; \hat{T}_1 + \hat{T}_2$. Projection of the Schrödinger equation on the HF determinant and excited determinants leads to **non-linear** equations for the coefficients t_i^a, t_{ij}^{ab} of the wavefunction. Energy:

$$E = \langle \Phi_{HF} | e^{-\hat{S}} \hat{H} e^{\hat{S}} | \Phi_{HF} \rangle = \langle \Phi_{HF} | \hat{H} e^{\hat{S}} | \Phi_{HF} \rangle \tag{11}$$

Coefficients:

$$\langle \Phi_I | e^{-\hat{S}} \hat{H} e^{\hat{S}} | \Phi_{HF} \rangle = \langle \Phi_I | \hat{H} e^{\hat{S}} | \Phi_{HF} \rangle = 0 \tag{12}$$

- No explicit wavefunction (infinite summation), density, orbitals and orbital energies.
- Method is size-consistent
- Approximations lead to CEPA–0, $(\mathrm{SC})^2$CI, Epstein-Nesbet perturbation theory.

X. HANDLING NON-DYNAMICAL CORRELATION

Orbitals should represent several determinants equally well. HF orbitals are the best orbitals for one single specific determinant. MCSCF (multi-configurational SCF) is the solution, as orbitals and CI coefficients for a selected number of states are optimized at the same time.

XI. PRINCIPLE OF MCSCF

Wavefunction:

$$|\Psi\rangle \;=\; \sum_m c_m \, |\Phi_m\rangle \tag{13}$$

Excitation operators:

$$\hat{E}_{ij} \;=\; (a_{i\alpha}^\dagger a_{j\alpha} + a_{i\beta}^\dagger a_{j\beta}) \tag{14}$$

With this the first-order density matrix is

$$D_{ij} \;=\; \langle\Psi|\hat{E}_{ij}|\Psi\rangle \;=\; \sum_{mn} c_m c_n D_{ij}^{mn} \tag{15}$$

and the second-order density matrix associated with the wavefunction is

$$P_{ijkl} \;=\; \frac{1}{2}\sum_{mn} c_m c_n \langle\Phi_m|\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}|\Phi_n\rangle \;=\; \sum_{mn} c_m c_n P_{ijkl}^{mn} \tag{16}$$

In the two cases the density matrices associated with each individual determinant is contracted to the overall densities.

The Hamiltonian is written in second quantization (independent of the electron number) as

$$H = \sum_{ij} h_{ij}\hat{E}_{ij} + \sum_{ijkl} g_{ijkl}(\hat{E}_{ij}\hat{E}_{kl} - \delta_{ik}\hat{E}_{jl}). \tag{17}$$

With these preliminaries the total energy is written in compact form as

$$E = \sum_{ij} h_{ij}D_{ij} + \sum_{ijkl} g_{ijkl}\,P_{ijkl}. \tag{18}$$

where the one-electron and 2-electron-integrals, h_{ij} and g_{ijkl}, depend only on the orbitals, and the one- and two-particle density matrices D_{ij} and P_{ijkl} depend only on the CI coefficients. The derivatives with respect to the coefficients can then be formed straightforward.

Conserving the norm of the wavefunction: write the wavefunction as an exponential of the anti-hermitian operator $\hat{T}$ ($\hat{T}^\dagger = -\hat{T}$)

$$|\Psi'\rangle = e^{\hat{T}}e^{\hat{S}}|\Psi\rangle \tag{19}$$

where $\hat{S}$ is an orbital-rotation operator and $\hat{T}$ the excitation operator, in order to pass from a MC wavefunction Ψ to a new function Ψ'.[1]

Energy:

$$E(\kappa, C) \;=\; \langle\Psi|e^{-\hat{S}}e^{-\hat{T}}\hat{H}e^{\hat{T}}e^{\hat{S}}|\Psi\rangle \tag{20}$$

Expansion to 2nd order through $e^x = \sum_{i=0}^{\infty} x^n/n!$:

$$E(T,S) \;=\; \langle\Psi|\hat{H} + [\hat{H},\hat{T}] + [\hat{H},\hat{S}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{2}[[\hat{H},\hat{S}],\hat{S}] + [[\hat{H},\hat{T}],\hat{S}] + \ldots|\Psi\rangle \tag{21}$$

showing the ingredients to calculate for an optimization procedure like the Newton-Raphson method using gradients and second derivatives.

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[1] Example a rotation operator between two orbitals:

$$\hat{S} = \begin{pmatrix} (\cos\kappa_{12})\,\hat{a}_1^\dagger\hat{a}_1 & -(\sin\kappa_{12})\,\hat{a}_1^\dagger\hat{a}_2 \\ (\sin\kappa_{12})\,\hat{a}_2^\dagger\hat{a}_1 & (\cos\kappa_{12})\,\hat{a}_2^\dagger\hat{a}_2 \end{pmatrix}$$

- Alternative: optimimzation of the total energy by alternating between orbital and CI-coefficient update until convergence.
- Analogon for the Hartree-Fock case: Singles-CI and iteration until satisfaction of Brillouin's theorem; $\langle \Phi_0 | \mathbf{H} | \Psi_i^a \rangle = F_{ia} = 0$ for that Φ_0 is a HF solution.
- CI-coefficients only for some determinants, orbitals including core orbitals.
- Starting orbitals: HF orbitals of a cation, adding to the orbital space the correct virtual orbitals of the obtained set → valence CI, for being able to judge on the quality of the orbitals. All states possible of the designed CI-space.
- CAS, complete active space. n electrons occupy N orbitals, Full-CI within this space. Wavefunction and density available, but no orbitals or orbital energies.
- Ionization energies: difference between n-electron WF and $n-1$-electron WF.

XII. STATE-SPECIFIC VERSUS STATE-AVERAGED MCSCF

Different problems:

- Dissociation from closed shell to open shells (nightmare: $\mathrm{Cr}_2 \longrightarrow 2\ \mathrm{Cr}$ with 12 open shells)
- Multiplet and transition states of a transition metal complex

The first remains a singlet, so only one state is of interest. Orbitals are optimized for that state.

In the second the use of different orbitals for different states may introduce systematic error. One should use one single orbital set optimized for all states.

XIII. COMBINING NON-DYNAMICAL AND DYNAMICAL CORRELATION

To the CAS space excitations from the core to the CAS or from the CAS to the virtual space can be added → dynamical correlation. States within the reference space: P-space; outside: Q-space. Effect different on different states in the P-sapce, due to symmetry or flexibility of the basis set (MR-CI). Same size-consistence defect as for single-reference case.

A. Perturbation theory

Basic problem: what is the reference energy for the denominators $E_n^{(0,P)} - E_m^{(0,Q)}$? Barycentric solution: $E_{ref} = (1/n) \sum_{i=1}^{n} E_i^{(0)}$ All perturbing states must be outside the energy interval spanned by the reference states (intruder problem).

XIV. WHAT PROPERTIES CAN WE CALCULATE

MCSCF provides a density, and as well MR-CISD.

A. Properties based on total energy

Spin states, IR spectra, geometries, polarizabilities, thermochemistry
Difference between different states: photo-absorption spectra, singlet-triplet optical transitions, ionization potentials, spin flip

B. Other properties

Ionicities, electron density, multipolar moments, continuous dissociation curves, concurrent bond breaking

XV. A HELPFUL APPROXIMATION: PSEUDOPOTENTIALS

A. Frozen-core approximation

Freezing core electrons in the correlation treatment is equivalent to modifying the nuclear repulsion and the one-electron part of the hamiltonian. The Fock matrix is invariant, and as well the total energy

$$F_{\alpha\beta} = \underbrace{h_{\alpha\beta} + \sum_{k\in core} 2(\alpha\beta|kk) - (\alpha k|k\beta)}_{h'_{\alpha\beta}} + \sum_{k\in valence} 2(\alpha\beta|kk) - (\alpha k|k\beta) \tag{22}$$

With the modified integrals all correlation calculations can be performed, with less operations. Indices run over valence orbitals only.

B. Model potentials

Valence orbitals have the full nodal structure; the model potential simplifies the calculation through fitting procedures (Coulomb operator) and application to atoms before a full calculation. The model potential operator is added to the Fock operator.

C. Pseudopotentials

Operators $\hat{V}$ to be added to the Fock matrix. Semilocal form

$$V_{\mathrm{PP}}(r) \;=\; \underbrace{-\frac{Z - Z_{\mathrm{core}}}{r}}_{\text{Coulomb term}} + \underbrace{\sum_i d_i\, r^{n_i}\, e^{-a_i\, r^2}}_{\text{local term}} + \underbrace{\sum_\ell \left(\sum_i d_{i,\ell}\, r^{n_{i,\ell}}\, e^{-a_{i,\ell}\, r^2}\right) |P_\ell\rangle \langle P_\ell|}_{\text{semi-local term}} \tag{23}$$

Valence orbitals do not have the nodes to be orthogonal on the core orbitals. Shape consistent potentials: orbitals are made to ressemble the best the all-electron orbitals (Durand-Barthelat, Hay-Wadt in GAUSSIAN). Publications in the 80s, no developments any more. Energy-consistent potentials: different atomic states are reproduced (Dolg-Preuss or Stuttgart-Dresden-Cologne). Developments still for actinides with partial f occupations.