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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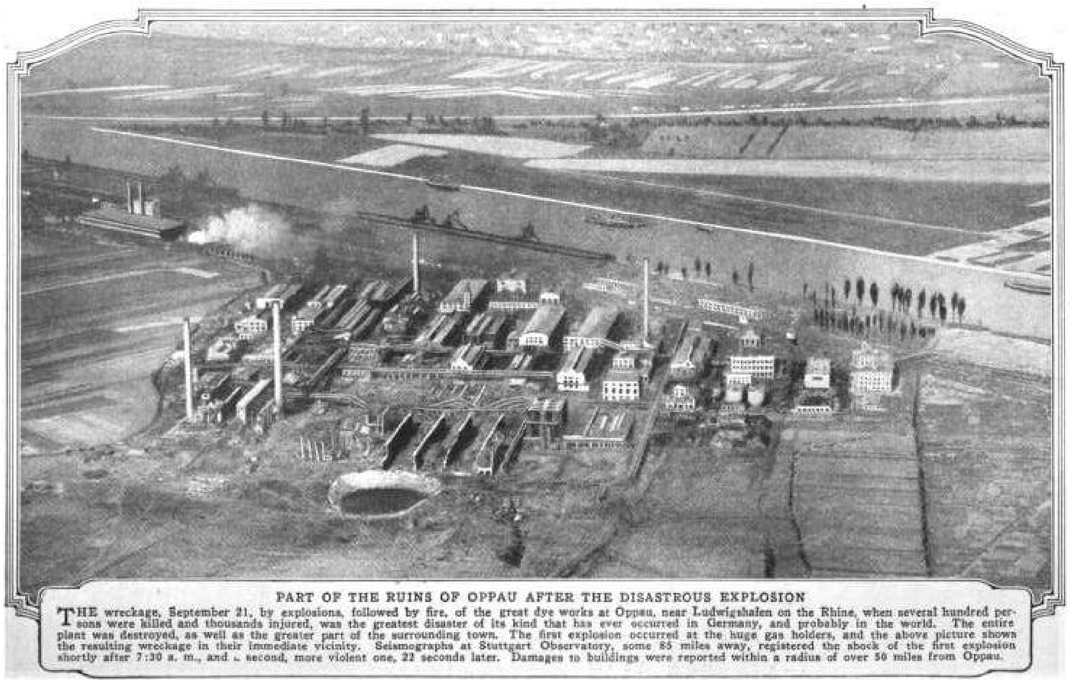
I. WHY THEORETICAL (QUANTUM) CHEMISTRY

- 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

$$\hat{H}\,\Psi \;=\; E\,\Psi \qquad (1)$$

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

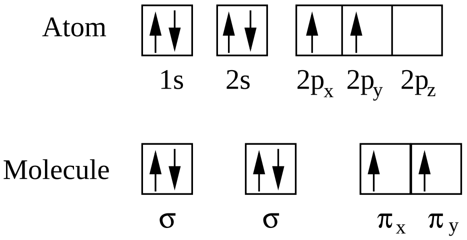
"The general theory of quantum mechanics is now complete... The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known."

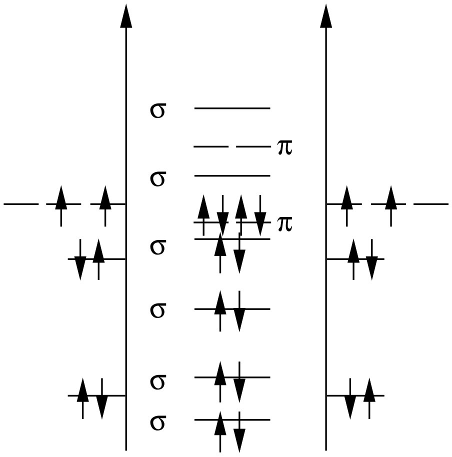
P.A.M. Dirac "Quantum Mechanics of Many-Electron Systems", Proc.R.Soc.Lond. **A123** (1929) 714-733

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

A wavefunction must be normalized and anti-symmetric with respect to an exchange of two electrons. A Slater determinant, built from occupied (spin-)orbitals

$$\Psi(\vec{r}_1,\sigma_1,\vec{r}_2,\sigma_2,\ldots,\vec{r}_2,\sigma_n) \;=\; \frac{1}{\sqrt{n!}}\begin{vmatrix} \phi_1(\vec{r}_1)\chi_1(\sigma_1) & \phi_1(\vec{r}_2)\chi_1(\sigma_2) & \ldots & \phi_1(\vec{r}_n)\chi_1(\sigma_n) \\ \phi_2(\vec{r}_1)\chi_2(\sigma_1) & \phi_2(\vec{r}_2)\chi_2(\sigma_2) & \ldots & \phi_2(\vec{r}_n)\chi_2(\sigma_n) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_n(\vec{r}_1)\chi_n(\sigma_1) & \phi_n(\vec{r}_2)\chi_n(\sigma_2) & \ldots & \phi_n(\vec{r}_n)\chi_n(\sigma_n) \end{vmatrix} \tag{2}$$

for fixed positions of the nuclei (Born-Oppenheimer approximation, justified by the mass difference of electrons and protons) obeys to the two conditions. $\phi_i(\vec{r})$ is a function in space at point $\vec{r}$, and $\chi_i(\sigma)$ a spin function with a formal variable σ. χ_i can be either α or β. Thus an electron does not "have" a spin 'up' or 'down' for it's entire life, but delivers 'up' when being in a spin-orbital with $\chi(\sigma)=\alpha$ and 'down' when in a spin-orbital with $\chi(\sigma)=\beta$.

The spatial part of the orbitals are linear combinations of "atomic orbitals" or "basis functions":

$$\phi_i(\vec{r}) \;=\; \sum_\alpha c_{\alpha\, i}\,\varphi_\alpha(\vec{r}) \tag{3}$$

Linear combinations of Slater determinants $\Psi=\sum_I c_I\,\Phi_I$ are still anti-symmetric and can be used as wavefunctions.

V. EXCURSION TO ORTHOGONALITY

In order to speak of a norm, we have to introduce a scalar product and a notion of orthogonality. We need a set of numbers (scalars), usually complex numbers $c=a+ib$, a vector space with an operation "+" (elements of the vector space should satisfy (x+y)+z = x+(y+z), x+y=y+x, existence of a neutral element and an inverse), and multiplication of a scalar with a vector. A scalar product takes two vectors, and produces a scalar, again with necessary rules: $(x, y) = (y, x)^*$, $(x, \mu y + \lambda z) = \mu(x, y) + lambda(x, z)$, $(x, x) \geq 0$, and $= 0$ only if x is the neutral element ("zero" vector).

In our case, orbitals or determinants span respective vectors spaces, and the scalar product is defined as the "overlap integral"

$$(f, g) := \int f(x)\, g(x)\, dx$$

where x runs over all variables as arguments of f and g.

Orthogonal means that the integral is exactly zero, and normalized stands for an integral (f, f) equal to one.

VI. TWO-ELECTRON WAVEFUNCTIONS

For 2 electrons we can separate the wavefunction into a space and a spin part. With one determinant

$$\begin{aligned}
\Psi^S(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) &= \frac{1}{\sqrt{2}}\phi(\vec{r}_1)\phi(\vec{r}_2)\left(\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)\right) \\
\Psi^T_1(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) &= \frac{1}{\sqrt{2}}\left(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\right)\alpha(\sigma_1)\alpha(\sigma_2) \\
\Psi^T_{-1}(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) &= \frac{1}{\sqrt{2}}\left(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\right)\beta(\sigma_1)\beta(\sigma_2) \qquad (4)
\end{aligned}$$

and with two determinants

$$\begin{aligned}
\Psi^S(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) &= \frac{1}{\sqrt{2}}\left(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) + \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\right) \times \frac{1}{\sqrt{2}}\left(\alpha\beta - \beta\alpha\right) \\
\Psi^T_0(\vec{r}_1, \sigma_1, \vec{r}_2, \sigma_2) &= \frac{1}{\sqrt{2}}\left(\phi_1(\vec{r}_1)\phi_2(\vec{r}_2) - \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\right) \times \frac{1}{\sqrt{2}}\left(\alpha\beta + \beta\alpha\right)
\end{aligned} \qquad (5)$$

We wrote as shorthand $\alpha\beta - \beta\alpha$ for $\alpha(\sigma_1)\beta(\sigma_2) - \beta(\sigma_1)\alpha(\sigma_2)$, and we see that the three functions Ψ^T_i have all the same (anti-symmetric) spatial part, but different spin parts.

VII. TOTAL ENERGY

$$E \;=\; \langle\Psi|\hat{H}|\Psi\rangle \quad \text{but not} \quad \hat{H}\,\Psi \;=\; E\,\Psi \qquad (6)$$

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 equation, 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.

VIII. HARTREE-FOCK EQUATIONS

Total energy for one single determinant (closed shell case):

$$\begin{aligned} E &= 2\sum_{i\in occ.} h_{ii} + \sum_{i,j\in occ.} \left(2(ii|jj) - (ij|ij)\right) \\ &= \sum_{\alpha,\beta} P_{\alpha\beta} h_{\alpha\beta} + \frac{1}{4}\sum_{\alpha,\beta} P_{\alpha\beta}\left(\sum_{\gamma,\delta} P_{\gamma\delta}\left(2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta)\right)\right) \end{aligned}$$

- Density matrix $P_{\alpha\beta} = 2\sum_{i\in occ.} c_{\alpha i}\, c_{\beta i}$ in a (finite) basis $\phi_i(\vec{r}) = \sum_\alpha c_{\alpha i}\chi_\alpha(\vec{r})$.
- We have to derive E wrt the $c_{\alpha i}$ under the condition

$$\delta_{ij} = \langle\phi_i|\phi_j\rangle = \sum_{\alpha\beta} c_{\alpha i}\, c_{\beta j}\, S_{\alpha\beta}$$

$$\frac{\partial}{\partial c_{\gamma i}}\sum_{\alpha\beta} P_{\alpha\beta} h_{\alpha\beta} = 4\, c_{\gamma i} h_{\gamma\gamma} + 2\sum_{\beta\neq\gamma} c_{\beta i} h_{\beta\gamma} + 2\sum_{\beta\neq\gamma} c_{\beta i} h_{\gamma\beta} = 4\sum_\beta c_{\beta i} h_{\gamma\beta}$$

Lagrange multipliers ϵ :

$$\mathcal{L} = E - 4\sum_{ij}\epsilon_{ij}\left(\sum_{\alpha\beta} c_{\alpha\, i} c_{\beta\, j}\, S_{\alpha\beta} - \delta_{ij}\right)$$

leads to equations

$$\begin{aligned} 0 &= \frac{\partial}{\partial c_{\alpha i}}\mathcal{L} \\ &= 4\sum_\beta c_{\beta i}\underbrace{\left(h_{\alpha_\beta} + \sum_{\gamma\delta} P_{\gamma\delta}\left(2(\alpha\beta|\gamma\delta) - (\alpha\delta|\gamma\beta)\right)\right)}_{\text{Fock matrix } F_{\alpha\beta}} - 4\sum_j\sum_\beta \epsilon_{ij}\, c_{\beta j}\, S_{\alpha\beta} \end{aligned}$$

In matrix form:

$$F\,C \;=\; S\;C\;\epsilon$$

or

$$F\,\phi_i \;=\; \sum_j \epsilon_{ij}\,\phi_j$$

beyond the limitations of a (finite) basis set to express molecular orbitals ϕ_i

- Self-consistent (F contains the occupied orbitals ϕ_i) eigenvalue problem
- Orbitals for lowest energy within single-determinant wavefunction
- Unitary rotations ($U^\dagger = U^{-1}$) within the occupied or the virtual orbital space do not change the energy of wavefunction.
- Transform orbitals for ϵ diagonal: canonical orbitals

$$F\,\phi_i \;=\; \epsilon_i\,\phi_i$$

- Brillouin's theorem: occupied and virtual orbital do not mix: $F_{ia} = 0$ for any set of Hartree-Fock orbitals (canonical or not).

IX. BASIS SETS

Hydrogen atom: spans not all possible space of one-electron functions.

- Nodeless Slater functions

$$\phi^{\mathrm{STF}}_{n\ell m}(r,\theta,\varphi;\alpha) \; = \; Y_{\ell m}(\theta,\varphi) \times r^{n-1} \times e^{-\beta\, r} \qquad \ell \leq n-1$$

- Gaussian functions

$$\phi^{\mathrm{GTF}}_{\ell m}(r,\theta,\varphi;\alpha) \; = \; Y_{\ell m}(\theta,\varphi) \times r^{\ell} \times e^{-\alpha\, r^2}$$

Why Gaussians ? Try to calculate a four-center bielectronic integral

$$\int\int \frac{e^{-\alpha|\vec{r}_1-\vec{R}_A|}e^{-\beta|\vec{r}_1-\vec{R}_B|}e^{-\gamma|\vec{r}_2-\vec{R}_C|}e^{-\delta|\vec{r}_2-\vec{R}_D|}}{|\vec{r}_1-\vec{r}_2|}d^3r_1d^3r_2$$

Possible with Gaussians due to product formula

$$e^{-a(\vec{r}-\vec{R}_A)^2}e^{-b(\vec{r}-\vec{R}_B)^2} = e^{-\frac{ab}{a+b}(\vec{R}_A-\vec{R}_B)^2}e^{-(a+b)(\vec{r}-\frac{a\vec{R}_A+b\vec{R}_B}{a+b})^2}$$

transforming a 4-center integral into a 2-center integral.

- Minimal basis sets: for each atomic occupied level a set of basis functions (H $1s$, C $1s2s2p$, Ti $1s2s2p3s3p3d4s$ etc.)
- Split-valence basis sets: multiple basis functions for each valence orbital (6-31G, double or triple ζ etc.)
- Even-tempered basis sets: Gaussian exponents obey geometrical law $\alpha_i = \alpha_0 \times \tau^i$
- add polarization functions of higher angular momentum
- add diffuse functions with small exponents for bond formation
- add correlation functions
- ... ... toward complete basis set.

Basis set libraries: `https://bse.pnl.gov/bse/portal` Basis Set Exchange with ≈ 500 basis sets.

- Nearly every quantum chemistry program has its library

X. 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

XI. WHAT PROPERTIES CAN WE CALCULATE

- Total energy $\longrightarrow$ 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 $\longrightarrow$ density, multipolar moments, population analysis, atomic basins
- Orbital energies $\longrightarrow$ excitation energies, ionization potentials, electron affinities

XII. 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 electronic 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**

XIII. 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.

XIV. PRINCIPLE OF MCSCF

Wavefunction:

$$|\Psi\rangle \;=\; \sum_m c_m\,|\Phi_m\rangle \tag{7}$$

Excitation operators:

$$\hat{E}_{ij} \;=\; (a^\dagger_{i\alpha}a_{j\alpha} + a^\dagger_{i\beta}a_{j\beta}) \tag{8}$$

With this the first-order density matrix is

$$D_{ij} \;=\; \langle\Psi|\hat{E}_{ij}|\Psi\rangle \;=\; \sum_{mn} c_m c_n D^{mn}_{ij} \tag{9}$$

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

$$P_{ijkl} \;=\; \frac{1}{2}\sum_{mn} c_m c_n \langle\Phi_m|\hat{E}_{ij}\hat{E}_{kl} - \delta_{jk}\hat{E}_{il}|\Phi_n\rangle \;=\; \sum_{mn} c_m c_n P^{mn}_{ijkl} \tag{10}$$

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

$$H = \sum_{ij} h_{ij}\hat{E}_{ij} + \sum_{ijkl} g_{ijkl}(\hat{E}_{ij}\hat{E}_{kl} - \delta_{ik}\hat{E}_{jl}). \tag{11}$$

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

$$E = \sum_{ij} h_{ij}D_{ij} + \sum_{ijkl} g_{ijkl}\,P_{ijkl}. \tag{12}$$

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 $\hat{T}$ ($\hat{T}^\dagger = -\hat{T}$)

$$|\Psi'\rangle = e^{\hat{T}} e^{\hat{S}} |\Psi\rangle \tag{13}$$

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:

$$E(\kappa, C) \;=\; \langle\Psi|e^{-\hat{S}}e^{-\hat{T}}\hat{H}e^{\hat{T}}e^{\hat{S}}|\Psi\rangle \tag{14}$$

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

$$E(T,S) \;=\; \langle\Psi|\hat{H} + [\hat{H},\hat{T}] + [\hat{H},\hat{S}] + \frac{1}{2}[[\hat{H},\hat{T}],\hat{T}] + \frac{1}{2}[[\hat{H},\hat{S}],\hat{S}] + [[\hat{H},\hat{T}],\hat{S}] + \dots|\Psi\rangle \tag{15}$$

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

- Alternative: optimization 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.

XV. 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.

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[1] Example: a rotation operator between two orbitals:

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