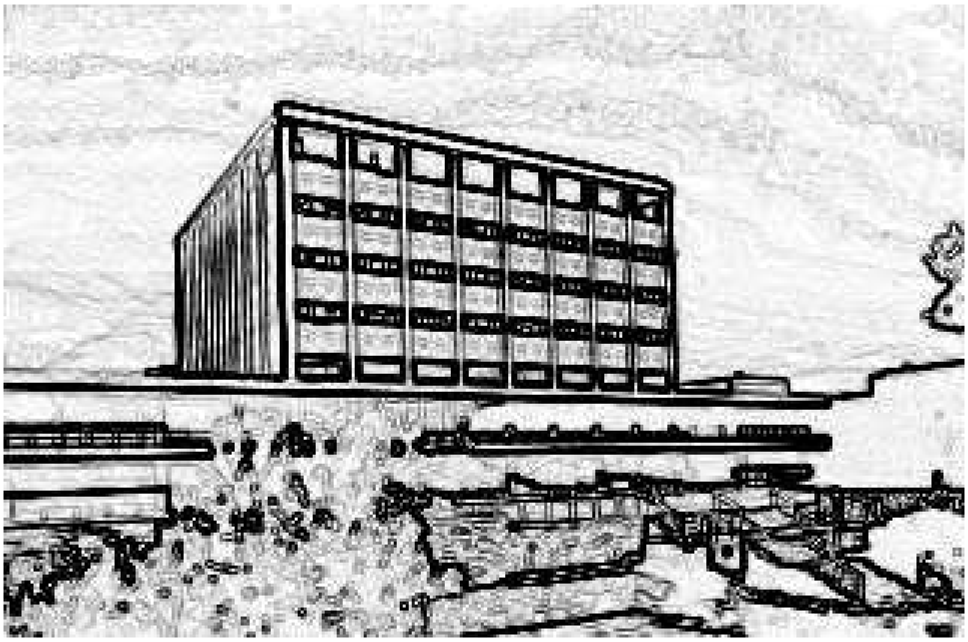
DFT lite.



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Towards Density Functional Theory.

- **The general problem** :

  Determine the *energy spectrum* and the corresponding *wavefunctions* of a system of M electrons bound by a skeleton of N nuclei.

- **A reasonable simplification** :

  Solve the *electronic problem* quantum–mechanically in the *frozen frame* of the nuclear skeleton. (**Born and Oppenheimer**).

- **The mathematical apparatus** :

  Given a *self–adjoint Hamiltonian* H associated with the above problem, determine its *Eigenvalues* E_i and *Eigenstates* Ψ_i as follows (**Ritz**):

$$\begin{aligned} E_i &= \sup_{\Psi_i} | < \Psi_i | H \Psi_i > | \\ ||\Psi_i|| &= 1 \qquad \Psi_i \perp \Psi_1, \ldots, \Psi_{i-1} \end{aligned}$$

Still pondering ... :

- **The Hamiltonian** :

$$
\begin{aligned}
H &= \sum_{i}^{M} -\frac{1}{2}\nabla_i^2 + \sum_{i>j}^{M} \frac{1}{|\vec{r}_i - \vec{r}_j|} - \sum_{i,n}^{M,N} \frac{Z_n}{|\vec{r}_i - \vec{R}_n|} \\
&= E_{kin} + E_{el.-el.} + E_{el.-nuc.}
\end{aligned}
$$

- **Antisymmetric trial wavefunction** :

1. Guess a wavefunction (**Hylleraas, Bethe**).
2. Assume a **linear combination of determinantal wavefunctions**, avoiding **Gruppenpest** (**Slater**):

$$
\begin{aligned}
\Psi_i &= \Psi_i(\vec{r}_1, ..., \vec{r}_M) = \sum_{l} c_l \Phi_i^l(\vec{r}_1, ..., \vec{r}_M) \\
\Phi_i^l(...) &= \left(\frac{1}{M!}\right)^{\frac{1}{2}} \begin{vmatrix} \psi_1(\vec{r}_1) & \psi_2(\vec{r}_1) & ... & \psi_M(\vec{r}_1) \\ \psi_1(\vec{r}_2) & \psi_2(\vec{r}_2) & ... & \psi_M(\vec{r}_2) \\ ... & ... & ... & ... \\ \psi_1(\vec{r}_M) & \psi_2(\vec{r}_M) & ... & \psi_M(\vec{r}_M) \end{vmatrix}
\end{aligned}
$$

where $(\psi_i)_{i=1...}$ is an **orthonormal set of functions**.

First Nightmare :

- Guess a **reasonable wave function** :

$$\Psi_i = \Psi_i(\vec{r}_1, ..., \vec{r}_M; p_1, ..., p_K)$$

where the p_j denote a **set of trial parameters**.

- Try to **optimize** the set of parameters *analytically* and/or by *educated guess* (**Bethe**):

$$\frac{\partial}{\partial p_l}\left[\frac{< \Psi_i|H\Psi_i >}{< \Psi_i|\Psi_i >}\right] = 0 \qquad \forall l$$

- This works for **simple** wavefunctions and a **small** set of parameters, only.

- Use a *computer* (**Metropolis**).

1. **Energy functional** :

$$E(p_1, ..., p_k) = \left[\frac{< \Psi_i | H \Psi_i >}{< \Psi_i | \Psi_i >}\right]$$

2. Let your computer generate **sets of random configurations** :

$$\vec{p^i} = (p_1^i, ..., p_k^i) \qquad i = 0, 1, 2, ...$$

3. Introduce a **temperature** T.

4. **Accept** a configuration $\vec{p^i}$, if :

$$E(\vec{p^i}) < E(\vec{p}^{(i-1)})$$

5. **Reject** a configuration $\vec{p^i}$, if :

$$E(\vec{p^i}) > E(\vec{p}^{(i-1)}) \qquad \textbf{and (!)}$$
$$\exp\left(-\frac{E(\vec{p^i}) - E(\vec{p}^{i-1})}{KT}\right) < R$$

where R is a **random number** picked from $[0, 1]$.

6. **Keep sampling** your systems while **lowering the temperature** T, until below a given threshold T_0.

- Accurate, simple and **tedious**.

Second Nightmare :

- **Hamilton matrix elements** :

$$
\begin{aligned}
<\Phi_i^l|H\Phi_i^l> &= \int \Phi_i^{l*}(\vec{r}_1,...,\vec{r}_M)H\Phi_i^l(\vec{r}_1,...,\vec{r}_M)dV_1...dV_M \\
&= \sum_s \int \psi_s^*(\vec{r}) \left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\vec{r}-\vec{R}_n|}\right]\psi_s(\vec{r})dV \\
&+ \frac{1}{2}\sum_{s,t}\int \frac{\psi_s^*(\vec{r})\psi_s(\vec{r})\psi_t^*(\vec{r}')\psi_t(\vec{r}')}{|\vec{r}-\vec{r}'|}dVdV' \\
&- \frac{1}{2}\sum_{s,t}\int \frac{\psi_s^*(\vec{r})\psi_t(\vec{r})\psi_t^*(\vec{r}')\psi_s(\vec{r}')}{|\vec{r}-\vec{r}'|}dVdV'
\end{aligned}
$$

- Assume $\Psi_i = \sum_l c_l \Phi_i^l$. Then the Ritz variational principle boils down to **solving a matrix equation** :

$$
\begin{aligned}
\frac{\partial}{\partial c_{l'}}\left[<\Psi_i|H\Psi_i> - E_i(<\Psi_i|\Psi_i> - 1)\right] &= 0 \\
\Longrightarrow \quad \sum_l <\Phi_i^{l'}|H\Phi_i^l> c_l - E_i c_{l'} &= 0
\end{aligned}
$$

Give it a trial !

- **The recipe** :
  1. Transform to H in *spherical coordinates*.
  2. Use *complete set of states* :

     $$\phi_{nlm}(\vec{r}) = L_n(r)Y_{lm}(\theta, \phi)$$

     where the $L_n(r)$ are *Laguerre–Polynominals*, and the $Y_{lm}(\theta, \phi)$ are *Spherical Harmonics*.
  3. Use *Gaussian integration* and/or the *Wigner–Eckart–theorem* to evaluate integrals.
- You need **a little bit of patience** :
  1. *Enormous* number of integrals.
  2. *Giant* matrices :
     (Has anyone in the audience ever diagonalized more than a non–blocked 4x4–matrix by hand?)
- **Bingo**, you will **set the benchmarks** for quantum chemistry.

This suggests that :

- **Progress** in quantum chemistry is the sum of **two** factors :
  1. Improved *theoretical* concepts.
  2. Improved *hardware*, *storage capacities*, *software*.
- Depending on the *actual computing power*, it is often advisable to **jump back and forth** among different theoretical concepts.
- **Question :** Given *21st century computer technology*, could we **close** the theoretical part of this talk right here ?

An **obvious but wrong** guess would be the following :

The more **accurate** the methods, the more **computationally demanding** they are.

The rebutal of this statement won **Kohn** the 1998 Nobel Prize in Chemistry.

What did we overlook so far ?

- Not every *complete orthogonal set of functions* is of any **practical use**.
- **The reason** : *Quite trivially*, numerics are never able to benefit from more than **a finite subspace** of any infinite space of functions.
- **Our goal** : Generate **optimized** finite subspaces that *minimize* the total electronic Hamiltonian effectively.

Introduce **local potentials**, the *workhorses* of modern quantum chemistry.

- They are related to *hermitian one–particle operators* :

$$\underbrace{\left(-\frac{1}{2}\nabla^2 + v_{loc}(\vec{r})\right)}_{h_{loc}(\vec{r})} \psi_i(\vec{r}) = \epsilon_i \psi_i(\vec{r})$$

- A **system composed of such particles** would be described by the Hamiltonian :

$$H = \sum_i h_{i;loc} = \sum_i \left(-\frac{1}{2}\nabla_i^2 + v_{loc}(\vec{r}_i)\right)$$

- The corresponding wavefunction could be as simple as a **single Slater determinant**.

$\Longrightarrow$ How to obtain local potentials that build a reasonably small set of Slater determinants, **minimizing the exact electronic Hamiltonian** effectively ?

Hartree–Fock theory :

- Assume Ψ being **a single Slater determinant** composed of a set of orthonormal orbitals ψ_i.
- **Rayleigh–Ritz** to obtain *ground state* :

$$\frac{\delta}{\delta\psi_i^*}\left[\underbrace{<\Psi|H|\Psi>}_{E(\Psi)} - \sum_{ij}\lambda_{ij}[<\psi_i|\psi_j> -1]\right] = 0$$

- This leads to a set of **one–particle equations** :

$$\begin{aligned}
h_{hf}\psi_i &= (t + v_{ext} + v_{hart} + v_{ex})\psi_i = \lambda_i\psi_i \\
(t + v_{ext})\psi_i &= (-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\vec{r} - \vec{R}_n|})\psi_i(\vec{r}) \\
v_{hart}\psi_i &= \sum_j \int \frac{\psi_j^*(\vec{r}')\psi_j(\vec{r}')}{|\vec{r} - \vec{r}'|} dV' \psi_i(\vec{r}) \\
v_{ex}\psi_i &= -\sum_j \int \frac{\psi_j^*(\vec{r}')\psi_i(\vec{r}')}{|\vec{r} - \vec{r}'|} dV' \psi_j(\vec{r})
\end{aligned}$$

- This set of equations has to be solved **self–consistently**. This is **terribly slow**, and the results are only **moderately accurate** !
- **Corrections** : Perturbation theory (MP2,MP4,**Pople**), linear combination of Slater determinants (CI).

Slater X_α theory :

- Use **local exchange potential** as a substitute for Hartree–Fock exchange potential :

$$v_{ex}(\vec{r}) = \alpha \left(\sum_j \psi_j^*(\vec{r}) \psi_j(\vec{r}) \right)^{\frac{1}{3}} = \alpha \int \rho^{\frac{1}{3}}(\vec{r})$$

- **Exchange–potential is functional of one–particle density** $\rho(\vec{r})$.
- Exchange energy is **exact** for a homogeneous electron gas (**LDA–Approximation**). $\Longrightarrow$ *Reasonable !?!?!*
- **Considerably faster** than Hartree–Fock. Accuracy is comparable (assuming **total electronic energy is Hartree–Fock energy**).
- The latter point was massively criticized by **Kohn** and **Sham**, who derived a slightly different set of equations **Kohn–Sham method (DFT)**.
- I **disagree** with Kohn and Sham : Functional–integral techniques, Coupled Cluster method are **backing** Slater's Ansatz. And : it can be corrected systematically !

Kohn–Sham theory (DFT) :

- Apply LDA to **exchange–(correlation) energy** (!) :

$$E_{xc} = \int \beta \left(\sum_j \psi_j^*(\vec{r}) \psi_j(\vec{r}) \right)^{\frac{4}{3}} dV = \beta \int \rho^{\frac{4}{3}}(\vec{r}) dV$$

- Assume Ψ single Slater determinat composed of a set of orthonormal functions ψ_i
- **Rayleigh–Ritz** to obtain *ground state* :

$$\frac{\delta}{\delta \psi_i^*} \left[\underbrace{< \Psi | H | \Psi >}_{E(\rho)} - \sum_{ij} \lambda_{ij} [< \psi_i | \psi_j > -1] \right] = 0$$

- Set of **one–particle equations**:

$$\begin{aligned} h_{hf} \psi_i &= (t + v_{ext} + v_{hart} + v_{ex}) \psi_i = \lambda_i \psi_i \\ v_{ex}(\vec{r}) &= \frac{4}{3} \beta \rho^{\frac{1}{3}}(\vec{r}) \end{aligned}$$

- All **modern density functionals** were developed on the basis of this **prototype**.
- DFT is **reasonably fast** and **reasonably accurate** for most applications (*atoms, clusters, solids*).
- **Corrections** : Gradient corrections, spin–polarized DFT, nonlocal DFT. **Limited usefulness !**

Practical details :

- **Basis functions** ϕ_α $(\alpha = 1, ..., K)$:

$$\psi_i(\vec{r}) = \sum_\alpha c_i^\alpha \phi_\alpha(\vec{r})$$

- **Basis sets :**

1. Plane Waves :

$$\phi_\alpha(\vec{r}) = \exp(i\vec{k_\alpha} \cdot \vec{r})$$

2. Slater type function :

$$\phi_\alpha(\vec{r}) = \exp -(d_\alpha|\vec{r} - \vec{R_A}|)$$

3. Gaussians :

$$\phi_\alpha(\vec{r}) = \exp -(g_\alpha|\vec{r} - \vec{R_A}|^2)$$

- Eigenvalue problem $\Longrightarrow$ **Matrix equation** :

$$\begin{aligned} h_{loc}(\vec{r})\psi_i(\vec{r}) &= \epsilon_i\psi_i(\vec{r}) \\ \sum_\alpha c_i^\alpha < \phi_\beta|h_{loc}|\phi_\alpha > &= \epsilon_i \sum_\alpha c_i^\alpha < \phi_\beta|\phi_\alpha > \\ i &= 1, ..., K \end{aligned}$$

Ab initio simulations.

- **Structural optimizations** :

1. **Relaxed structure** :

$$\frac{\partial E_{tot}(\vec{R}_1^{\,0}, ..., \vec{R}_n^{\,0})}{\partial \vec{R}_n^{\,0}} = \vec{0} \qquad \forall n$$

where $E_{tot} = E_{0,el} + E_{nuc.-nuc.}$, i.e. the total electronic energy **plus** the repulsion between the nuclei.

2. Spectrum of matrix composed of second derivatives of E_{tot} (**Hesse–Matrix,** Hes) determines whether the configuration $(\vec{R}_1^{\,0}, ..., \vec{R}_n^{\,0}) = \vec{X}^0$ is a **maximum**, **minimum** or a **saddle point**.

3. One usually **guesses** a configuration where $\frac{\partial E_{tot}}{\partial \vec{R}_n^{\,i}} \neq \vec{0}$
$\Longrightarrow$ determine $\vec{X}^0$ **iteratively** (**Newton–Raphson, Broyden, Conjugate Gradient**).

4. Example (*unsophisticated move, Newton–Raphson*) :

$$\vec{X}^j - \vec{X}^i = -Hes^{-1}(\vec{X}^i)\frac{\partial E_{tot}}{\partial \vec{X}}(\vec{X}^i)$$

- *Combine* density functional theory with **molecular dynamics** $\Longrightarrow$ (**Car and Parrinello**).

Molecular Dynamics :

- **Lagrangian** for model system :

$$L = \frac{1}{2}\sum_i M_{(i)} \left(\frac{d\vec{r}_i}{dt}\right)^2 - \sum_{i<j} U(\vec{r}_{ij})$$

- **Equations of motion** $(\forall i)$:

$$\frac{d}{dt}\left(\frac{\partial L}{\partial(\frac{d\vec{r}_i}{dt})}\right) - \frac{\partial L}{\partial \vec{r}_i} = 0$$

$$M_{(i)}\left(\frac{d^2\vec{r}_i}{dt^2}\right) = -\frac{\partial U}{\partial \vec{r}_i} = \vec{F}_i$$

(Newton Dynamics)

- *Integration* of equations of motion ($\frac{d^2x}{dt^2} = f(x, \frac{dx}{dt}, t)$, stepsize h) :

  1. *Predictor step :*

$$\begin{aligned} x(t+h) &= x(t) + h\frac{dx}{dt} + h^2 \sum_{i=1}^{k-1} \alpha_i f(t+(1-i)h) \\ h\frac{dx}{dt}(t+h) &= x(t+h) - x(t) \\ &+ h^2 \sum_{i=1}^{k-1} \alpha'_i f(t+(1-i)h) \end{aligned}$$

  2. *Evaluate* $f(x, \frac{dx}{dt}, t+h)$.
  3. *Corrector step :*

$$\begin{aligned} x(t+h) &= x(t) + h\frac{dx}{dt} + h^2 \sum_{i=1}^{k-1} \beta_i f(t+(2-i)h) \\ h\frac{dx}{dt}(t+h) &= x(t+h) - x(t) \\ &+ h^2 \sum_{i=1}^{k-1} \beta'_i f(t+(2-i)h) \end{aligned}$$

- *Properties* (Units : $M_{(i)} = 1, k_B = 1, ...$) :

$$\begin{aligned} T &= \frac{1}{d(=2)N_a} < \sum_i \left(\frac{d\vec{r}_i}{dt}\right)^2 > \\ PV &= N_a T + \frac{1}{d(=2)} < \sum_i \vec{r}_i \cdot \vec{F}_i > \end{aligned}$$

- *Velocity rescaling* :

$$\left(\frac{d\vec{r}_i}{dt}\right)' = \frac{d\vec{r}_i}{dt} * \left(\frac{T_{id}}{T}\right)^{\frac{1}{2}}$$

Quantum mechanical MD :

- Treat the nuclei as **classical particles** or as **semiclassical objects**.
- The potential U becomes **much more complicated**:

$$
\begin{aligned}
U(\vec{r_1},...,\vec{r_N}) &= \sum_{i<j} U_{nuc.-nuc.}(|\vec{r_i}-\vec{r_j}|) \\
&+ \min_{\psi} < \psi | H_{el.}(\vec{r_1},...,\vec{r_N}) | \psi > \\
H_{el.}(\vec{r_1},...,\vec{r_N}) &= \sum_{i} V_{nuc.-el.}(\vec{r_i}) + \textit{electronic terms}
\end{aligned}
$$

- **Forces** (generally) :

$$
\begin{aligned}
\vec{F_k} &= < \psi | \frac{\partial(\sum_i V_{nuc.-el.}(\vec{r_i}))}{\partial \vec{r_k}} | \psi > \\
&+ < \frac{\partial \psi}{\partial \vec{r_k}} | H_{el.} | \psi > + < \psi | H_{el.} | \frac{\partial \psi}{\partial \vec{r_k}} >
\end{aligned}
$$

- First term only $\rightarrow$ **Hellmann–Feynman**.
- All terms $\rightarrow$ **Pulay**.

Final remark :

Any idea what the successor of DFT might look like ?