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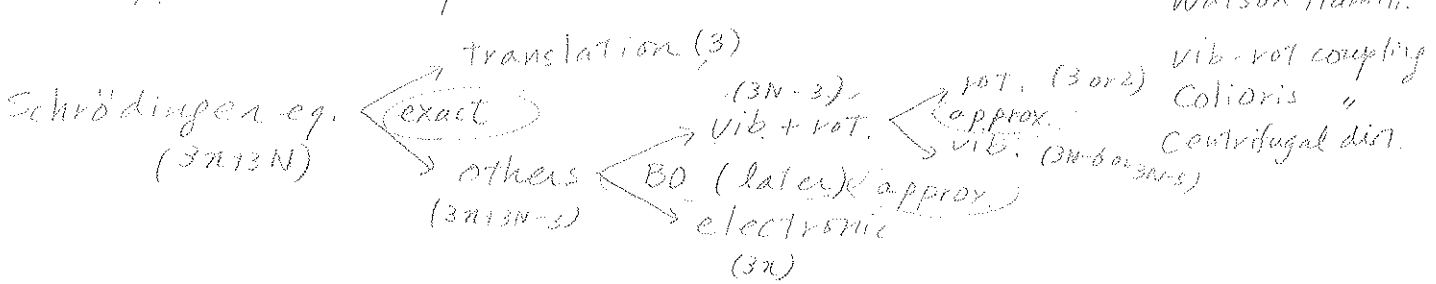
① Electronic structure theory

i) Born-Oppenheimer separation



$$\hat{H}\,\Psi(x_1, x_2, \cdots, x_N) = E\,\Psi(x_1, x_2, \cdots x_N)$$

$$\hat{H} = \sum_i^{\#e}\left(-\frac{1}{2}\nabla_i^2\right) - \sum_i^{\#e}\sum_I^{\#n}\frac{Z_I}{r_{iI}} + \sum_{i<j}^{\#e}\frac{1}{r_{ij}} + \sum_{I<J}^{\#n}\frac{Z_I Z_J}{r_{IJ}}$$

(Z_I: nuc. charge)

$\hat{H}_e$: $-\frac{1}{2}\nabla_i^2$ (kinetic), $-\sum\sum \frac{Z_I}{r_{iI}}$ (e-n distance), $\sum\sum \frac{1}{r_{ij}}$ (e-e distance)

$\sum\sum \frac{Z_I Z_J}{r_{IJ}}$: const. (r_{IJ}: n-n distance)

Sometimes we solve $\hat{H}_e\,\Psi = E_e\,\Psi$

$$E = E_{el} + \sum_{I<J}\frac{Z_I Z_J}{r_{IJ}}$$

ii) Antisymmetry / Pauli exclusion principle

$$\Psi(\cdots x_i \cdots x_j \cdots) = (-1)\,\Psi(\cdots x_j \cdots x_i \cdots)$$

spin-orbital coordinate $x_i = \{\underbrace{x_i, y_i, z_i}_{r_i}, \sigma_i\}$ (spin coordinate)

iii) Spin orbitals

$$\chi(x) = \phi(r)\,\alpha(\sigma) \quad \text{or} \quad \phi(r)\,\beta(\sigma)$$

(ϕ: spatial functions; α, β: spin functions)

$\langle \chi_i | \chi_j \rangle = \delta_{ij}$ is imposed usually

iv) Expansion of one- and multi-variable functions

$$f(x) = \sum_i c_i \eta_i(x)$$ always (possible as $\{\eta\}$ is complete / exact)

finding $f(x)$ is equivalent to finding $\{c\}$

$$g(x,y) = \sum_{ij} c_{ij} \eta_i(x) \eta_j(y)$$ also possible / exact as $\{\eta\}$ is complete

(because)

for a fixed value of $y = \bar{y}$, $g(x,\bar{y})$ is just a fxn of x

$$g(x,\bar{y}) = \sum_i c_i(\bar{y}) \eta_i(x)$$

coeffs are dependent on $\bar{y}$, thus a fxn of $\bar{y}$. Any fxn of $\bar{y}$ is expanded by $\{\eta\}$,

$$c_i(\bar{y}) = \sum_j c_{ij} \eta_j(\bar{y}).$$

leading to

$$g(x,\bar{y}) = \sum_{ij} c_{ij} \eta_i(x) \eta_j(\bar{y})$$

$$g(x,y,z) = \sum_{ijk} c_{ijk} \eta_i(x) \eta_j(y) \eta_k(z)$$ etc.

The product expansion is not the only way to expand a multi-variable fxn, (or not even exactly) the best way. Cf. R12 methods.

= most compact

v) Single determinant / Hartree-Fock method

The smallest number of products necessary to expand N-electron wave function (that satisfies antisym.) is N! that forms a determinant

$$|\Phi_0\rangle = \Phi_0(x_1, \cdots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(x_1) & \cdots & \chi_1(x_N) \\ \vdots & & \vdots \\ \chi_N(x_1) & \cdots & \chi_N(x_N) \end{vmatrix}$$

(x: spin orbital coordinate; $\frac{1}{\sqrt{N!}}$: normalization; χ_1: spinorbital)

determinant of spinorbitals = Slater determinant

$$= |\chi_1 \cdots \chi_N\rangle$$ (note this notation includes normalization coeff.)

Hartree-Fock (HF) method/approximation

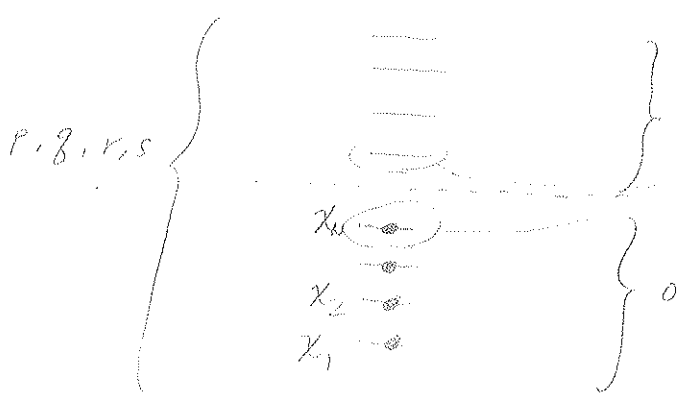
$$\min \frac{\langle \Phi_0 | \hat{H} | \Phi_0 \rangle}{\langle \Phi_0 | \Phi_0 \rangle} = E_{HF} \quad \text{by varying } \{\chi_i\}$$

which leads to effective one-electron eqns

$$\hat{f}(p)\chi_p(x_p) = \varepsilon_p \chi_p(x_p)$$

($\hat{f}$: Fock operator; ε_p: orbital energy)

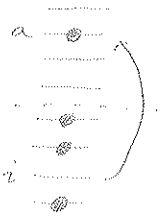
Spinorbitals $\{\chi_i\}$ with the N lowest ε_i's are used in $|\Phi_0\rangle$ (occupied)



vi) Multi-determinant / Configuration-interaction method

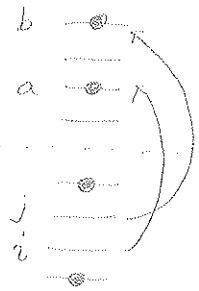
Singly excited determinant

$$|\Phi_i^a\rangle = |\chi_1 \cdots \chi_a \cdots \chi_N\rangle \qquad (\chi_i) \leftarrow \text{in } |\Phi_0\rangle$$



Doubly excited determinant

$$|\Phi_{ij}^{ab}\rangle = |\chi_1 \cdots \chi_a \cdots \chi_b \cdots \chi_N\rangle \qquad (\chi_i)\,(\chi_j) \text{ in } |\Phi_0\rangle$$



$$= (-1)\,|\chi_1 \cdots \chi_b \cdots \chi_a \cdots \chi_N\rangle = (-1)\,|\Phi_{ij}^{ba}\rangle$$

$$= (-1)\,|\chi_1 \cdots \underset{(\chi_j)}{\chi_a} \cdots \underset{(\chi_i)}{\chi_b} \cdots \chi_N\rangle = (-1)\,|\Phi_{ji}^{ab}\rangle$$

$$= |\chi_1 \cdots \underset{(\chi_j)}{\chi_b} \cdots \underset{(\chi_i)}{\chi_a} \cdots \chi_N\rangle = |\Phi_{ji}^{ba}\rangle$$

→ only $|\Phi_{ij}^{ab}\rangle$ $i<j$, $a<b$ are linearly independent basis functions ($i=j$ or $a=b$ → zero functions)

Exact N-electron wave function Ψ

$$|\Psi\rangle = c_0|\Phi_0\rangle + \sum_{i}^{\text{occ.}}\sum_{a}^{\text{virt.}} c_i^a |\Phi_i^a\rangle + \sum_{i<j}^{\text{occ.}}\sum_{a<b}^{\text{virt.}} c_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \sum_{i<j<k}^{\text{occ.}}\sum_{a<b<c}^{\text{virt.}} c_{ijk}^{abc} |\Phi_{ijk}^{abc}\rangle + \cdots + \sum_{i_1<i_2\cdots<i_N}^{\text{occ.}}\sum_{a_1<a_2<\cdots<a_N}^{\text{virt.}} c_{i_1\cdots i_N}^{a_1\cdots a_N} |\Phi_{i_1\cdots i_N}^{a_1\cdots a_N}\rangle$$

exact expansion!

Full Configuration interaction (FCI)

$$\min \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \text{ by varying } \{c\} \qquad (\{\chi_i\} \text{ may be HF orbitals but need not be})$$

$$= E_{FCI}$$

vii) Correlation energy

$E_{corr} = E_{FCI} - E_{HF}$ for a given basis function set to expand each χ_i.

In the limit # basis fxns $\to \infty$, E_{FCI} is the exact, non-relativistic, Born-Oppenheimer energy (exact solution of Schrödinger electronic eq.), E_{HF} is the so-called HF-limit energy.

viii) Electronic structure theories

ab initio (wave function) theory
Do not approximate $\hat{H}$ (after BO non-relativistic)
Approximate $|\Psi\rangle$, {c}

HF

CIS, CID, CISD, ... , FCI

CCD, LCCD, CCSD, CCSD(T), ... TCC

MP2, MP3, ... MP∞

MCSCF, CASSCF, CASPT2 ...

MRCI, MRCC, ...

EOM-CCSD, EOM-CCSDT ...

DMRG, MP2-R12, CCSD-R12

calibrated, assessed in comparison with FCI

semi-empirical theory
Approximate $\hat{H}$
Do not usually approximate $|\Psi\rangle$

Hückel, SSH
Ising, Hubbard
CNDO
INDO
MNDO
AM1, PM1
DFT (LDA, GGA, Hybrid)

calibrated, assessed in comparison with experiment or accurate ab initio results

in-between
DFT-based GW, RPA
SCS-MP2, SOS-MP2