Electronic structure

Hartree-Fock method in molecules and solids (1)

- Hermann Haken & Hans C. Wolf, *The Physics of Atoms and Quanta*, Springer, 2004
- Hermann Haken & Hans C. Wolf, *Molecular Physics and Elements of Quantum Chemistry*, Springer, 2003
- Attila Szabo & Neil Ostlund, *Modern Quantum Chemistry*, Dover, 1996

Yongle Li

Brief review of Quantum mechanics: Results of atoms

Electronic structure of atoms

$\hat{H} = \hat{T} + \hat{V}$ Typically, we prefer to discuss in position space.

$\hat{T} = \frac{1}{2m}\hat{\boldsymbol{p}}^2$ $\hat{\boldsymbol{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z)$ $\hat{p}_j = \frac{\hbar}{i}\frac{\partial}{\partial x_j}$ Basic example of vector operator

$\hat{V} = V(\boldsymbol{r})$

$$i\hbar\frac{\partial}{\partial t}\psi(\boldsymbol{r}, t) = \hat{H}\psi(\boldsymbol{r}, t)$$

In many cases, the hamiltonian does not contain time explicitly, so

$\psi(\boldsymbol{r}, t) = e^{-iEt/\hbar}\psi(\boldsymbol{r})$

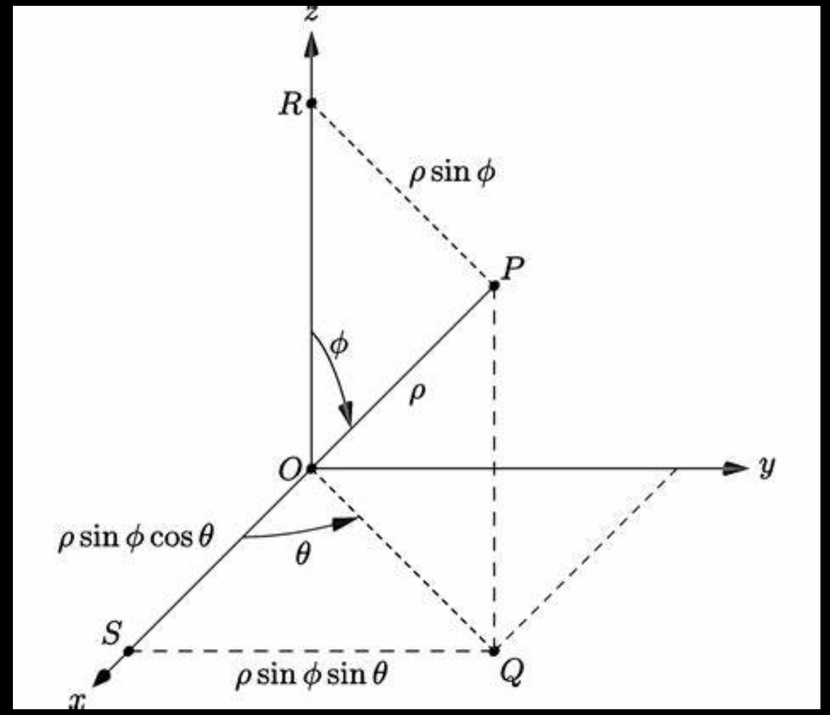
$$\hat{H}\psi_v(\boldsymbol{r}) = E_v\psi_v(\boldsymbol{r})$$

Quantum mechanical results of H-like Atom

$$\hat{H} = -\frac{\hbar^2}{2m_0}\nabla^2 - \frac{1}{4\pi\varepsilon_0}\frac{Ze^2}{r} \qquad \boldsymbol{r} = (r, \theta, \phi)$$

$$\psi_{nlm}(\boldsymbol{r}) = R_{nl}(r)P_l^m(\cos\theta)e^{im\phi}$$

$$E_n = -\frac{m_0 Z^2 e^4}{2\hbar^2(4\pi\varepsilon_0)^2}\frac{1}{n^2} = -\frac{13.6}{n^2}\ \text{eV}$$



$$F_{l,m}(\theta,\phi) \equiv P_l^m(\cos\theta)e^{im\phi}$$

$$Y_{l,m}(\theta,\phi)$$

Spherical harmonics
S. Hassani,
Mathematical Physics,
2nd edition, Springer,
2013, Chapter 13

$$l=0, \quad F_{0,0}=\frac{1}{\sqrt{4\pi}}$$

$$l=1, \quad F_{1,0}=\sqrt{\frac{3}{4\pi}}\cos\theta=\sqrt{\frac{3}{4\pi}}\frac{z}{r}$$

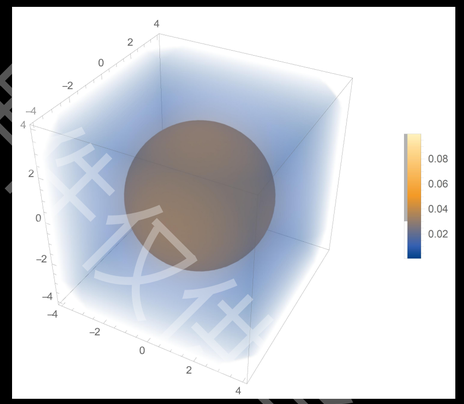
$$l=1, \quad F_{1,\pm1}=\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi} \Rightarrow \pm\sqrt{\frac{3}{8\pi}}\frac{x\pm y}{r}$$

$$\frac{(F_{1,1}+F_{1,-1})}{2}=\sqrt{\frac{3}{8\pi}}\frac{x}{r}$$

$$\frac{(F_{1,1}-F_{1,-1})}{2i}=\sqrt{\frac{3}{8\pi}}\frac{y}{r}$$

$F_{1,|1|}$, $F_{1,|1|}{}'$

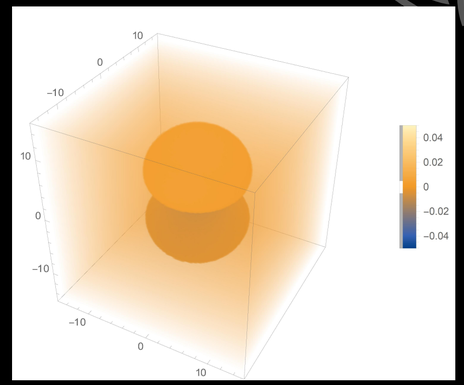
$n = 1,\ l = 0$



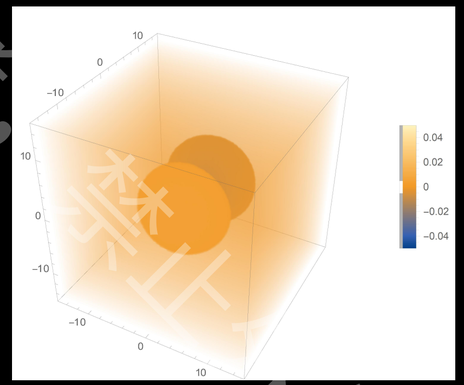
s: sharp
p: principal
d: diffuse
f: fundamental

Haken & Wolf,
The Physics of Atoms and Quanta,
Springer, 2010, pp. 176

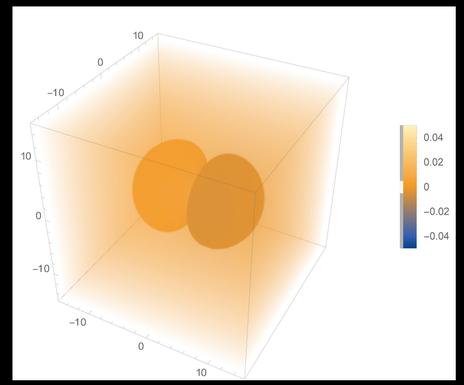
$n = 2,\ l = 1$



$m = 0$



$m = -1$



$m = 1$

$$R_{n,l} = N_{n,l} e^{-\kappa_n r} r^l L_{n+1}^{2l+1}(2\kappa_n r)$$

Here $N_{n,l}$ is a normalization factor, defined as:

$$\int_0^\infty R^2 r^2 \mathrm{d}r = 1$$

$$\kappa_n = -\frac{m_0 Z e^4}{\hbar^2 (4\pi\varepsilon_0)} \frac{1}{n}$$

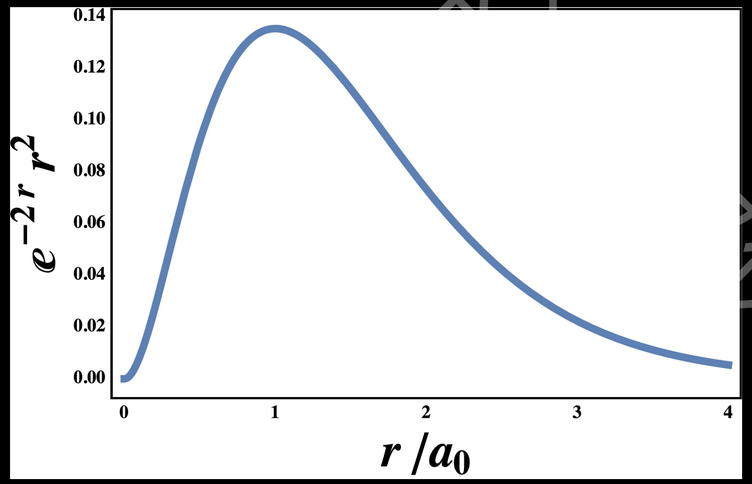
$$L_{n+1}^{2l+1}(\rho) \equiv \frac{\mathrm{d}^{2l+1}}{\mathrm{d}\rho^{2l+1}} L_{n+1}$$

A derivative of the *Laguerre polynomials* L_{n+1}

$$L_{n+1}(\rho) = e^\rho \frac{\mathrm{d}^{n+1}(e^{-\rho}\rho^{n+1})}{\mathrm{d}\rho^{n+1}}$$

Example: $L_1^1 = -1$

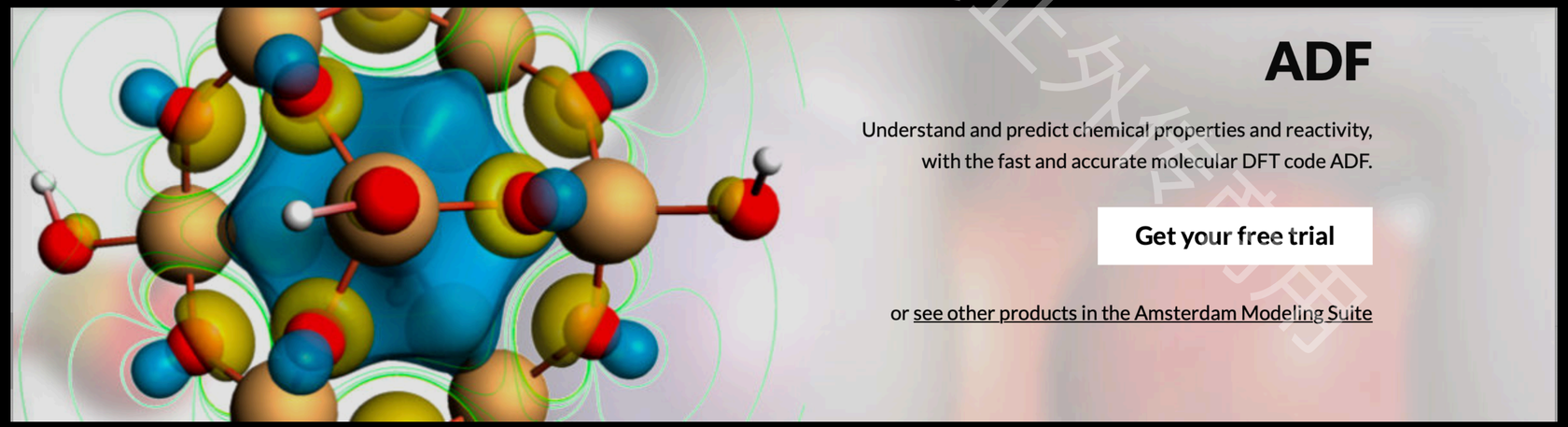
$$R_{1,0} = N e^{-\kappa_1 r}$$

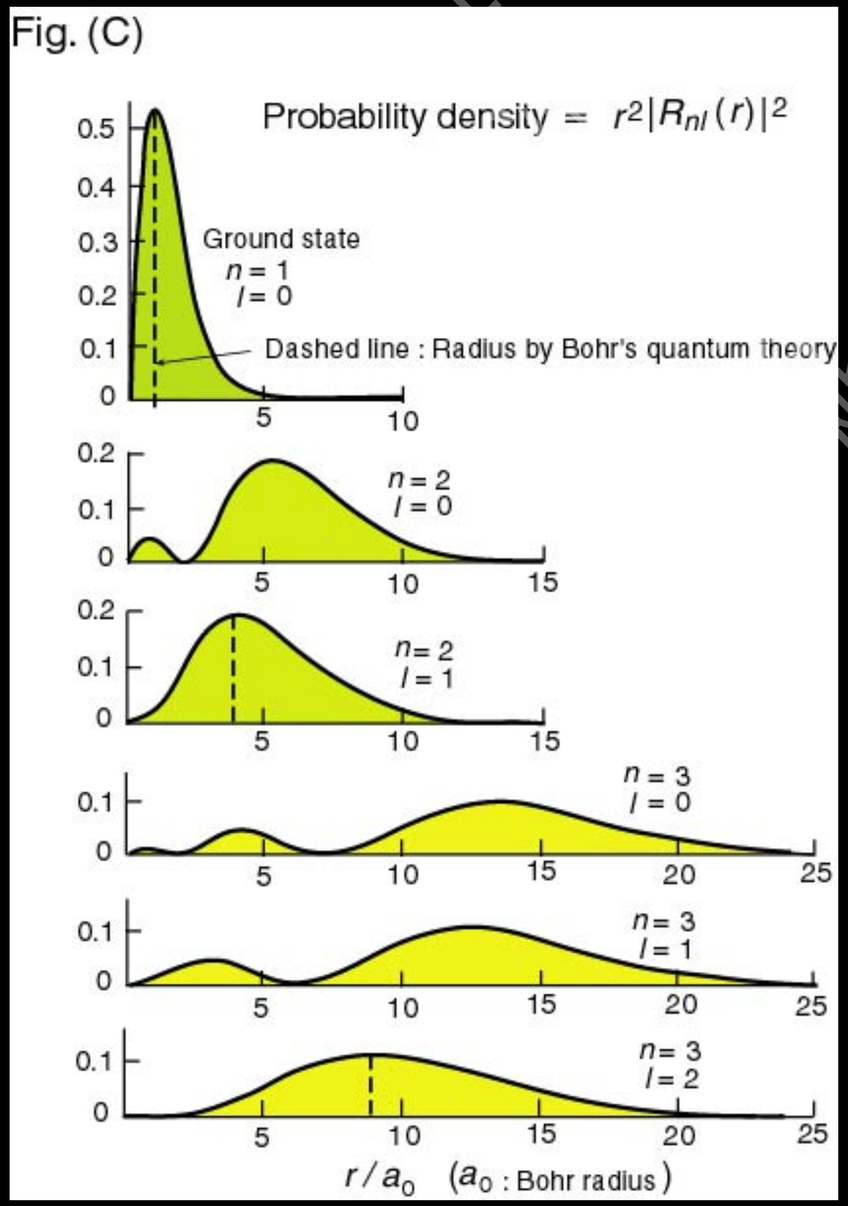


$$R_{1,0} = Ne^{-\kappa_1 r}$$

$$r^2|R_{1,0}|^2 = N^2 r^2 e^{-2\kappa_1 r}$$

In quantum chemistry, the first Laguerre polynomial is called *Slater Type Orbital* (STO).
It's used in ADF (Amsterdam Density Functional).





Internet Seminar

Microscopic World -2-

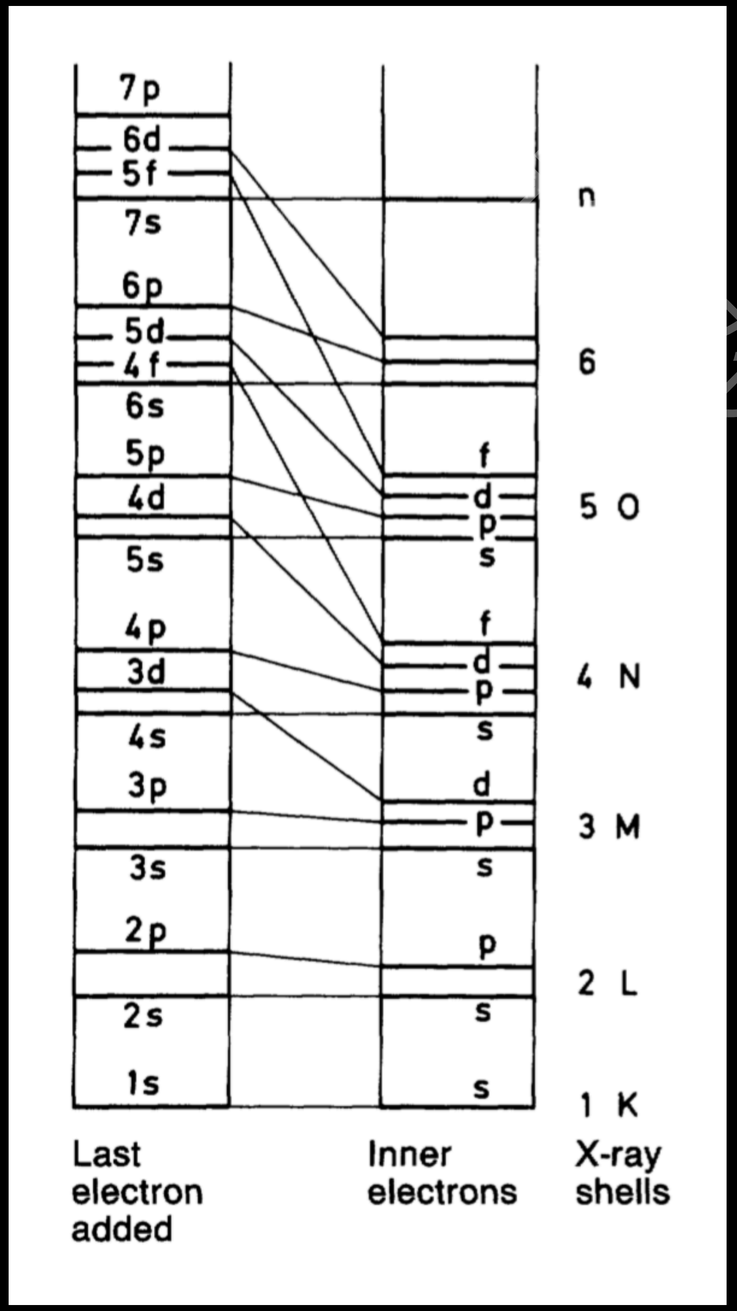
Introduction to Quantum Mechanics

Dr. Kenjiro Takada
Emeritus professor of Kyushu University

http://ne.phys.kyushu-u.ac.jp/seminar/MicroWorld2_E/2Part3_E/2P32_E/hydrogen_atom_E.htm

https://demonstrations.wolfram.com/HydrogenAtomRadialFunctions/

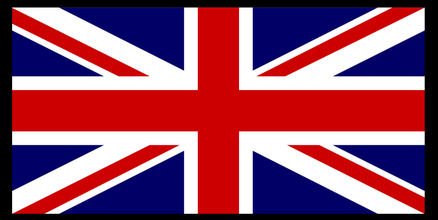
Electronic structure of many electron atoms



Hermann Haken & Hans C. Wolf, *The Physics of Atoms and Quanta*, Springer, 2004

Quantum mechanics for molecules

From brute-force to Hartree-Fock Self-Consistent Field



https://mathshistory.st-andrews.ac.uk/Biographies/Hartree/

https://physicstoday.scitation.org/do/10.1063/pt.6.6.20171222a/full/

Walter Ritz

Sion (Switzerland) February 22, 1878 – Göttingen July 7, 1909

Variational method

Published: 14 February 2018

The Deep Ritz Method: A Deep Learning-Based Numerical Algorithm for Solving Variational Problems

Weinan E & Bing Yu

Communications in Mathematics and Statistics **6**, 1–12 (2018) | Cite this article

The variation principle:

Given a normalized wave function $|\tilde{\Phi}\rangle$ that satisfies the appropriate boundary conditions, then the *expectation value* of the Hamiltonian is an *upper bound* to the exact ground state energy.

$$\langle\tilde{\Phi}|\tilde{\Phi}\rangle = 1$$

$$\langle\tilde{\Phi}|\hat{H}|\tilde{\Phi}\rangle \geq E_0 \quad \text{or} \quad \frac{\langle\tilde{\Phi}|\hat{H}|\tilde{\Phi}\rangle}{\langle\tilde{\Phi}|\tilde{\Phi}\rangle} \geq E_0$$

Once $|\tilde{\Phi}\rangle = |\Phi_0\rangle$ the identity holds.

Proof of the variation principle:
(With the help of completeness of basis)

$$\sum_{\alpha} |\Phi_\alpha\rangle\langle\Phi_\alpha| = 1$$

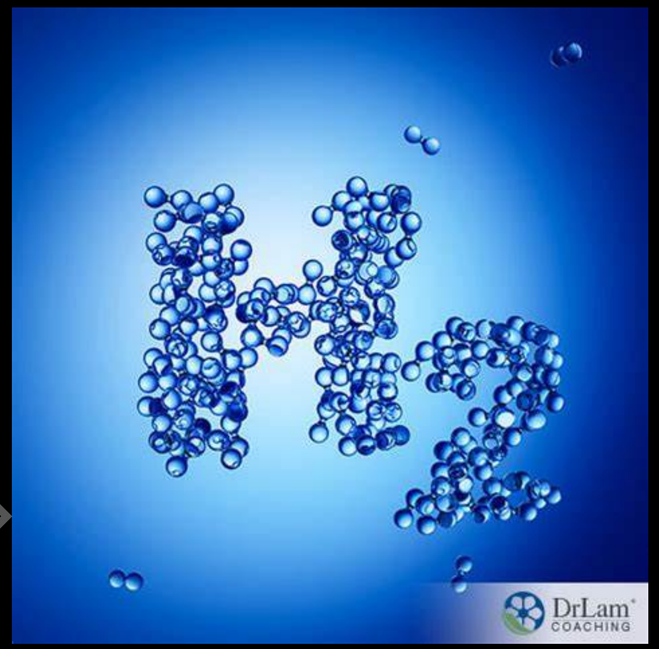
$$\langle\tilde{\Phi}|\tilde{\Phi}\rangle = 1 = \sum_{\alpha\beta} \langle\tilde{\Phi}|\Phi_\alpha\rangle\langle\Phi_\alpha|\Phi_\beta\rangle\langle\Phi_\beta|\tilde{\Phi}\rangle = \sum_{\alpha} |\langle\Phi_\alpha|\tilde{\Phi}\rangle|^2$$

$$\langle\tilde{\Phi}|\hat{H}|\tilde{\Phi}\rangle = \sum_{\alpha} \langle\tilde{\Phi}|\Phi_\alpha\rangle\langle\Phi_\alpha|\hat{H}|\Phi_\alpha\rangle\langle\Phi_\alpha|\tilde{\Phi}\rangle = \sum_{\alpha} E_\alpha |\langle\Phi_\alpha|\tilde{\Phi}\rangle|^2$$

$$\langle\tilde{\Phi}|\hat{H}|\tilde{\Phi}\rangle \geq \sum_{\alpha} E_0 |\langle\Phi_\alpha|\tilde{\Phi}\rangle|^2 = E_0 \sum_{\alpha} |\langle\Phi_\alpha|\tilde{\Phi}\rangle|^2 = E_0$$

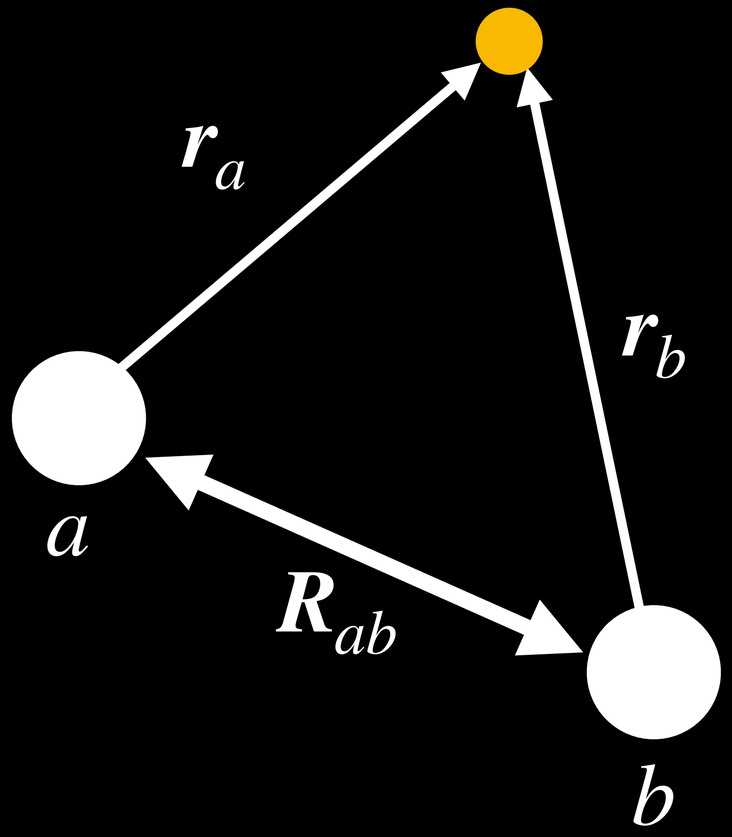
H_2^+

Step further: hydrogen molecular ion



Quantum mechanical treatment of H_2^+

Constructive interference: bonding state

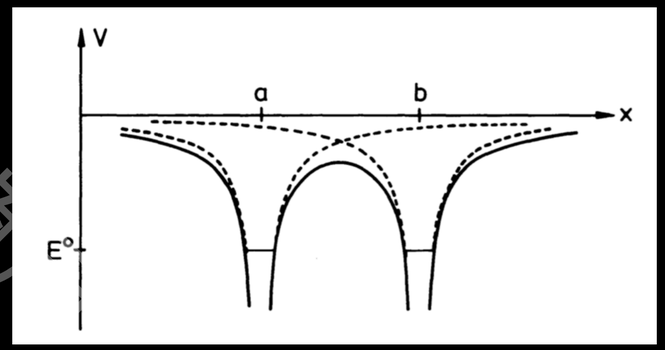


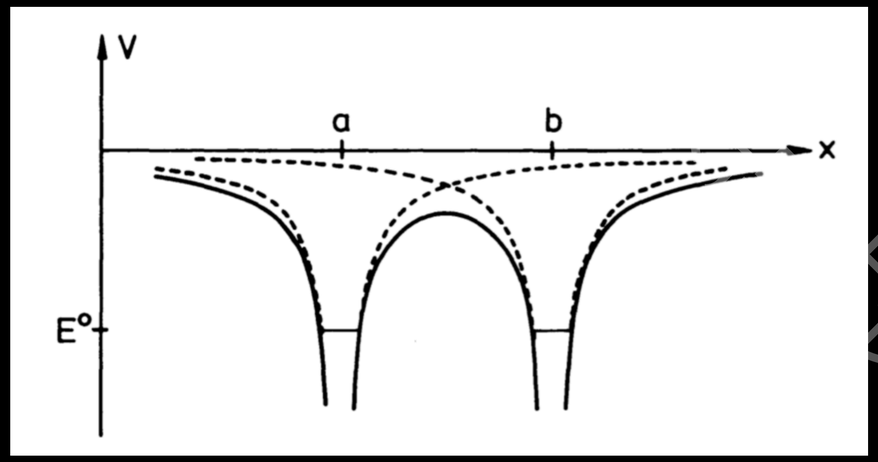
Starting point:
Atomic Schrödinger Equation

$$\hat{H}_\alpha \phi_\alpha(\boldsymbol{r}_\alpha) = \left(\frac{\hbar^2}{2m_0} \nabla^2 - \frac{1}{4\pi\varepsilon_0} \frac{e^2}{r_\alpha} \right) \phi_\alpha(\boldsymbol{r}_\alpha) = E_\alpha^0 \phi_\alpha(\boldsymbol{r}_\alpha)$$

$$\alpha = a, b$$

$$E_a^0 = E_b^0 = E^0$$





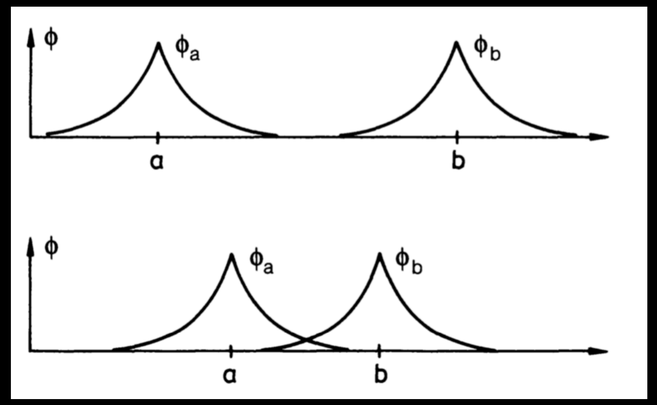
Molecular Schrödinger Equation

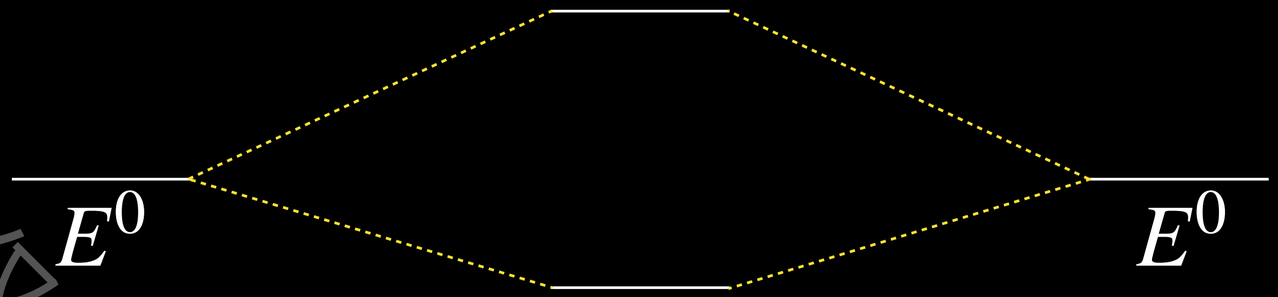
$$\left(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} - \frac{e^2}{4\pi\varepsilon_0 r_b}\right)\psi(\boldsymbol{r}_a, \boldsymbol{r}_b) = E\psi(\boldsymbol{r}_a, \boldsymbol{r}_b)$$

$$r_a = \sqrt{(R_{a,x} - x)^2 + (R_{a,y} - y)^2 + (R_{a,z} - z)^2}$$

$$r_b = \sqrt{(R_{b,x} - x)^2 + (R_{b,y} - y)^2 + (R_{b,z} - z)^2}$$

Guess:
Use atomic wave functions as building blocks!





ϕ_a ϕ_b

$$\psi = c_a\phi_a + c_b\phi_b$$

$$\hat{H}_a \left(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_a} - \frac{e^2}{4\pi\varepsilon_0 r_b} \right) c_a\phi_a +$$

$$\hat{H}_b \left(-\frac{\hbar^2}{2m_0}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r_b} - \frac{e^2}{4\pi\varepsilon_0 r_a} \right) c_b\phi_b$$

$$= E(c_a\phi_a + c_b\phi_b)$$

The atomic wave functions used here are also called *orbitals*.

$$\left(\underbrace{E^0 - E}_{\Delta E} - \frac{e^2}{4\pi\varepsilon_0 r_b}\right) c_a\phi_a + \left(\underbrace{E^0 - E}_{\Delta E} - \frac{e^2}{4\pi\varepsilon_0 r_a}\right) c_b\phi_b = 0$$

Left multiply $\langle a\,|\,\boldsymbol{r}\rangle$ (suppose we're using real functions):

$C, D \in \mathbb{R}$

$\langle a\,|\,\boldsymbol{r}\rangle = \phi_a^*(\boldsymbol{r})$

$$\langle\phi_a\,|\,\phi_b\rangle = S \neq 0 \quad \langle a\,|\,\frac{-e^2}{4\pi\varepsilon_0 r_b}\,|\,a\rangle = C \quad \langle a\,|\,\frac{-e^2}{4\pi\varepsilon_0 r_a}\,|\,b\rangle = D$$

$$\Delta E c_a + C c_a + \Delta E S c_b + D c_b = 0$$

$$\langle a\,|\,\hat{O}\,|\,b\rangle \equiv \int \mathrm{d}\boldsymbol{r}\ \phi_a^*(\boldsymbol{r})\hat{O}\phi_b(\boldsymbol{r})$$

$$(\Delta E + C)c_a + (\Delta E S + D)c_b = 0$$

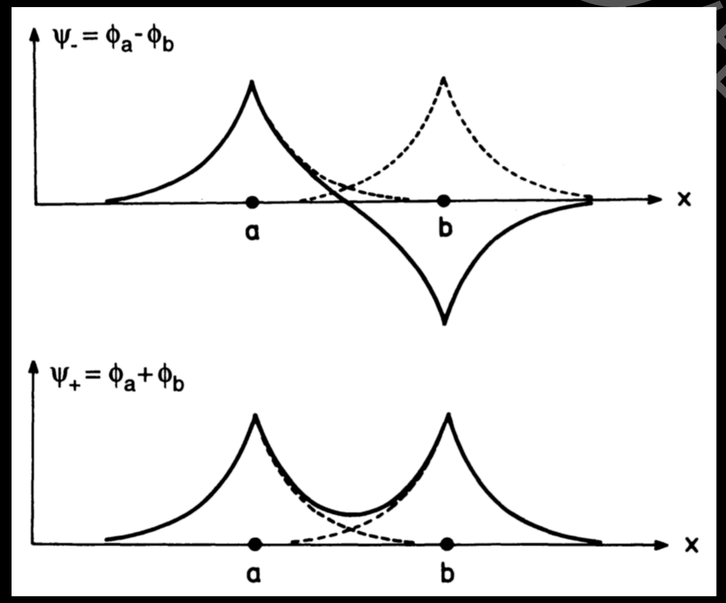
Left multiply $\langle b\,|\,\boldsymbol{r}\rangle$:

$$(\Delta E S + D)c_a + (\Delta E + C)c_b = 0$$

$$(\Delta E + C)c_a + (\Delta ES + D)c_b = 0$$

$$(\Delta ES + D)c_a + (\Delta E + C)c_b = 0$$

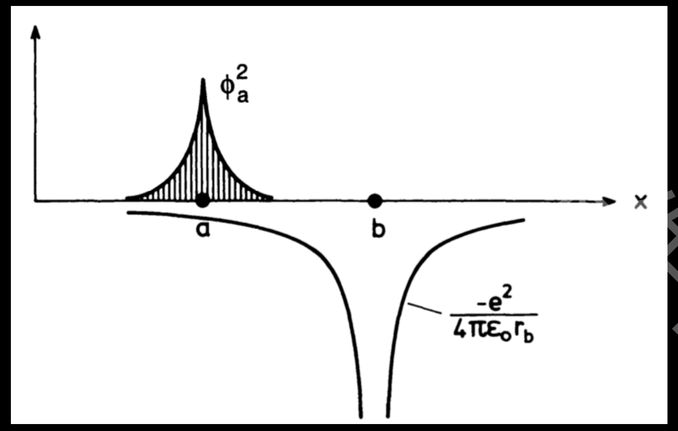
$$\Rightarrow (\Delta ES + D)^2 - (\Delta E + C)^2 = 0$$

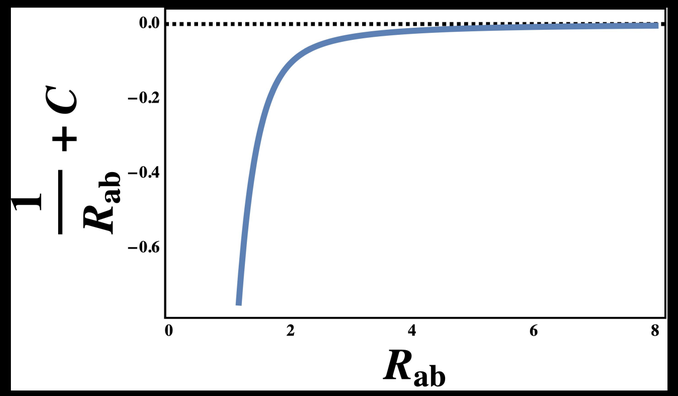


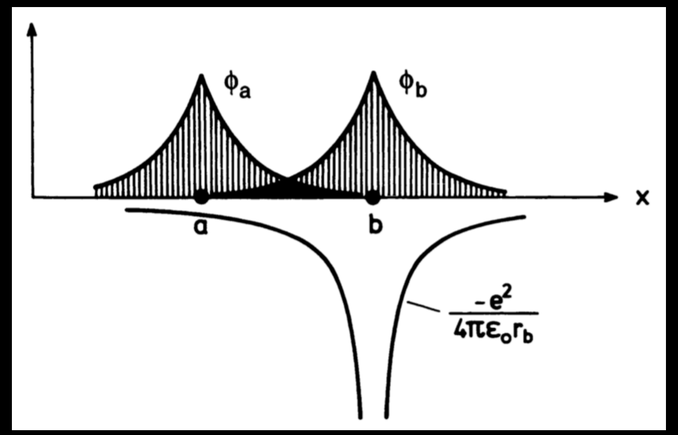
$$\Delta E_1 = E^0 + \frac{C - D}{1 - S} \quad \text{——}$$

$$\Delta E_2 = E^0 + \frac{C + D}{1 + S} \quad \text{——}$$

Here S is always small. So in later discussion, we can omit it.







$$\langle a | \frac{-e^2}{4\pi\varepsilon_0 r_b} | a \rangle = C$$

$$\boldsymbol{r}_a = \boldsymbol{R}_{ab} + \boldsymbol{r}_b$$

$$\boldsymbol{r}_b = \boldsymbol{r}_a - \boldsymbol{R}_{ab}$$

$$\phi_a(r) \propto e^{-\kappa r}$$

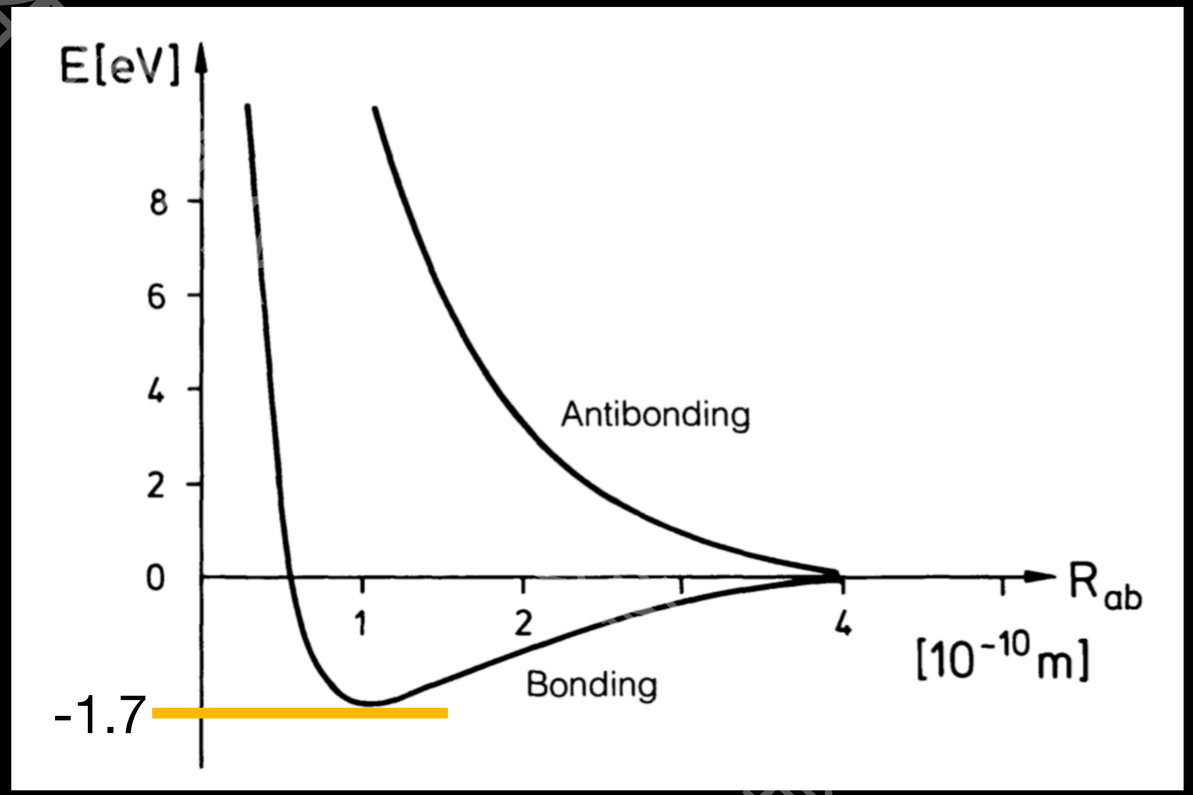
$$\frac{1}{r_b} = \frac{1}{|\boldsymbol{r}_a - \boldsymbol{R}_{ab}|} \approx \frac{1}{R_{ab}}(1 + \frac{r_b}{R_{ab}})$$

When R_{ab} is large, $C \approx -\frac{e^2}{4\pi\varepsilon_0 R_{ab}}$, this term counters the repulsion between the two protons.

$$\langle a | \frac{-e^2}{4\pi\varepsilon_0 r_a} | b \rangle = D$$

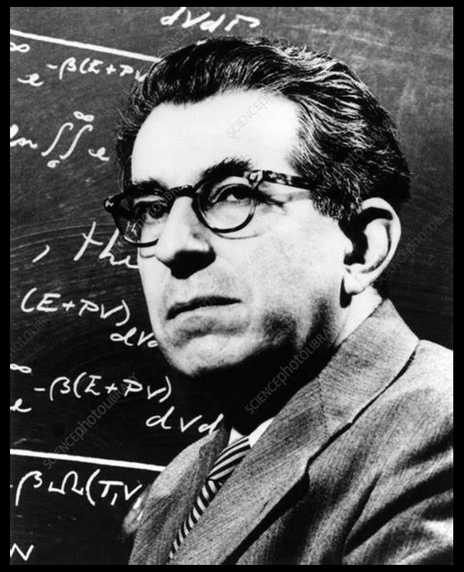
So the bonding mainly comes from the *exchange* term D, a *pure quantum* effect.

江元生，《结构化学》



Experimental value: −2.65 eV

	eV	kcal/mol
Calc.	-1.7	-39.2
Expr.	-2.65	-61.1

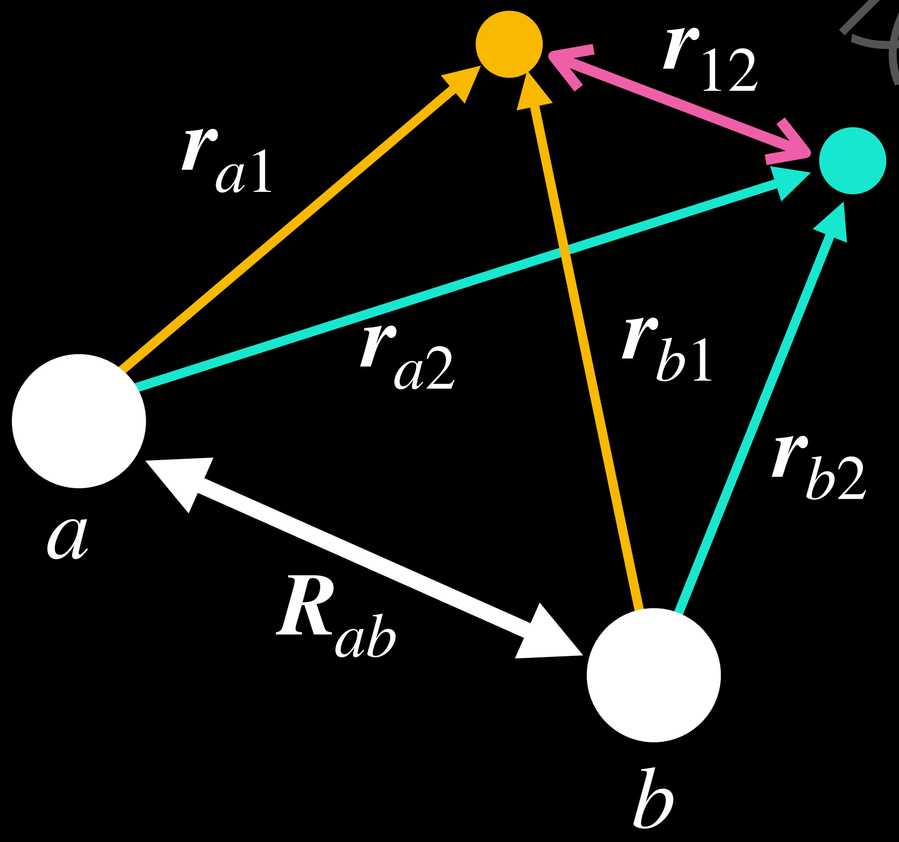


Step even further: hydrogen molecule

Walter Heinrich Heitler,
(2 January 1904 - 15 November 1981)
German physicist

Fritz Wolfgang London,
(March 7, 1900 - March 30, 1954)
German American physicist

H_2



$$\hat{H} = \boxed{-\frac{\hbar^2}{2m_0}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0 r_{a_1}}} \boxed{-\frac{\hbar^2}{2m_0}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_{b_2}}} - \frac{e^2}{4\pi\varepsilon_0 r_{b_1}} - \frac{e^2}{4\pi\varepsilon_0 r_{a_2}} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$\hat{H}\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$$

$$\left(-\frac{\hbar^2}{2m_0}\nabla_1^2 - \frac{e^2}{4\pi\varepsilon_0 r_{a_1}}\right)\phi_a(\boldsymbol{r}_1) = E^0\phi_a(\boldsymbol{r}_1)$$

$$\left(-\frac{\hbar^2}{2m_0}\nabla_2^2 - \frac{e^2}{4\pi\varepsilon_0 r_{b_2}}\right)\phi_b(\boldsymbol{r}_2) = E^0\phi_b(\boldsymbol{r}_2)$$

Pauli exclusion principle

The principle that two identical fermions cannot occupy the same quantum state in a body such as an atom.

— — Collins Encyclopedia

First, we need to consider the spin.

$$\langle \alpha(i) \,|\, \alpha(j) \rangle = \delta_{ij}$$

$$\langle \beta(i) \,|\, \beta(j) \rangle = \delta_{ij}$$

$$\langle \alpha(i) \,|\, \beta(j) \rangle = 0$$

$$\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) \Rightarrow \phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)\alpha(1)\alpha(2)$$

But the Hartree product does not fulfill the Pauli exclusion principle.

$$\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)\alpha(1)\alpha(2) - \phi_a(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_1)\alpha(2)\alpha(1)$$

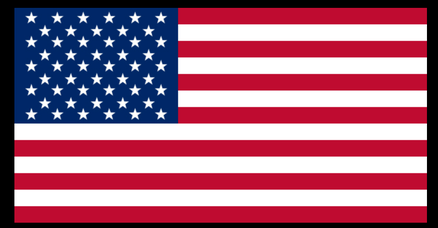
$$\Psi = \alpha(1)\alpha(2)\Psi_u(\boldsymbol{r}_1, \boldsymbol{r}_2) = \alpha(1)\alpha(2)\left[\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) - \phi_b(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)\right]$$

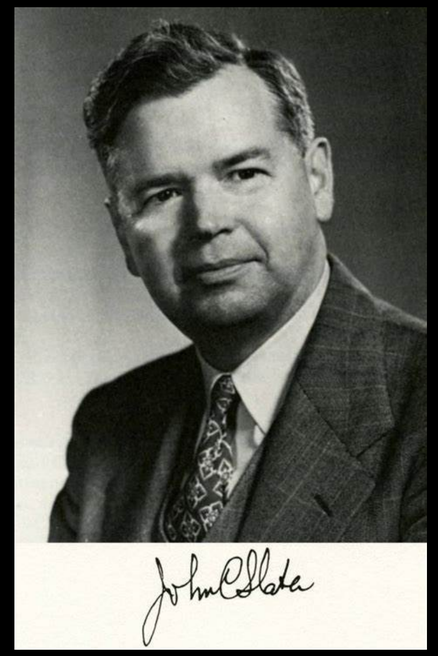
u: ungrade (Germany, odd)
g: grade (Germany, even)

Slater determinant

$$\Psi \propto \begin{vmatrix} \phi_a(\boldsymbol{r}_1)\alpha(1) & \phi_a(\boldsymbol{r}_2)\alpha(2) \\ \phi_b(\boldsymbol{r}_1)\alpha(1) & \phi_b(\boldsymbol{r}_2)\alpha(2) \end{vmatrix}$$

Standard tool for describing fermions.





(1900-1976)

All possibilities

$$\Psi = f_{\text{spin}}(1,2)\Psi_{g\text{ or }u}(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

$$\Psi = \alpha(1)\alpha(2)\Psi_u(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

$$\Psi = \beta(1)\beta(2)\Psi_u(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

$$\Psi = \frac{1}{2}\big(\alpha(1)\beta(2) + \alpha(2)\beta(1)\big)\Psi_u(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

Triplet

$$\Psi = \frac{1}{2}\big(\alpha(1)\beta(2) - \alpha(2)\beta(1)\big)\left[\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) + \phi_a(\boldsymbol{r}_2)\phi_b(\boldsymbol{r}_1)\right]$$

$$= \frac{1}{2}\big(\alpha(1)\beta(2) - \alpha(2)\beta(1)\big)\Psi_g(\boldsymbol{r}_1,\boldsymbol{r}_2)$$

Singlet

Heitler & London method

$$\hat{H}\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2) = E\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2)$$

Since there is no spin term in $\hat{H}$, we can just use Ψ_g and Ψ_u as trial solutions.

Here we use a concise notation, fix the first term as the function containing the position of the first electron, and the second term as the function containing the second electron.

$$\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) - \phi_b(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2) \equiv |ab\rangle - |ba\rangle$$

$$\langle \Psi | \Psi \rangle \equiv \iint |\Psi|^2 \, \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 \qquad \mathrm{d}^3 r \equiv \mathrm{d}x\mathrm{d}y\mathrm{d}z = r^2 \sin\theta \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi$$

$$\begin{aligned}\langle \Psi | \Psi \rangle &= \left[\langle ab| \pm \langle ba| \right] \left[|ab\rangle \pm |ba\rangle \right] \\ &= \langle ab|ab\rangle \pm \langle ab|ba\rangle \pm \langle ba|ab\rangle + \langle ba|ba\rangle\end{aligned}$$

$$\langle ab|ab\rangle = \langle a|a\rangle\langle b|b\rangle = 1 = \langle ba|ba\rangle$$

$$\langle ab|ba\rangle = \langle ba|ab\rangle = \langle a|b\rangle\langle b|a\rangle = |S|^2 = S^2$$

$$\langle \Psi | \Psi \rangle = 2(1 \pm S^2)$$

$$\frac{\langle \Psi_{g\,\text{or}\,u} | \hat{H} | \Psi_{g\,\text{or}\,u} \rangle}{\langle \Psi | \Psi \rangle} \geq E_{\text{ground}}$$

$$\big(\langle ab| \pm \langle ba| \big)\hat{H}\big(|ab\rangle \pm |ba\rangle \big)$$

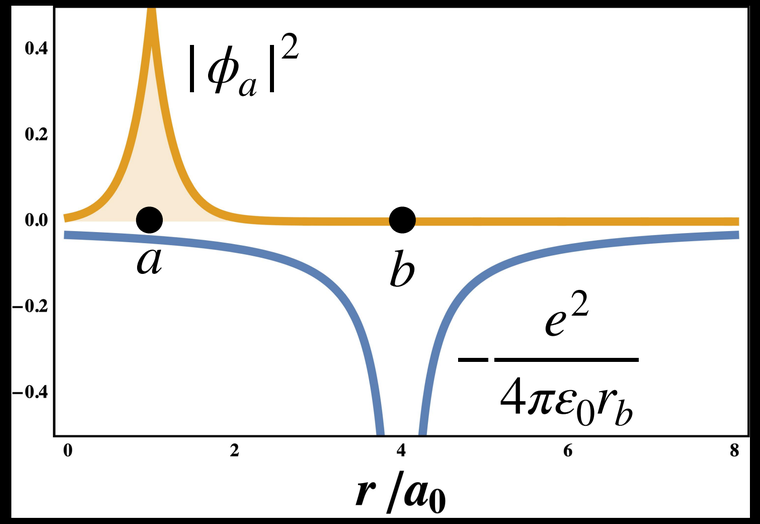
$$= 2\langle ab|\hat{H}|ab\rangle \pm 2\langle ab|\hat{H}|ba\rangle$$

$$\langle ab|\hat{H}|ab\rangle$$

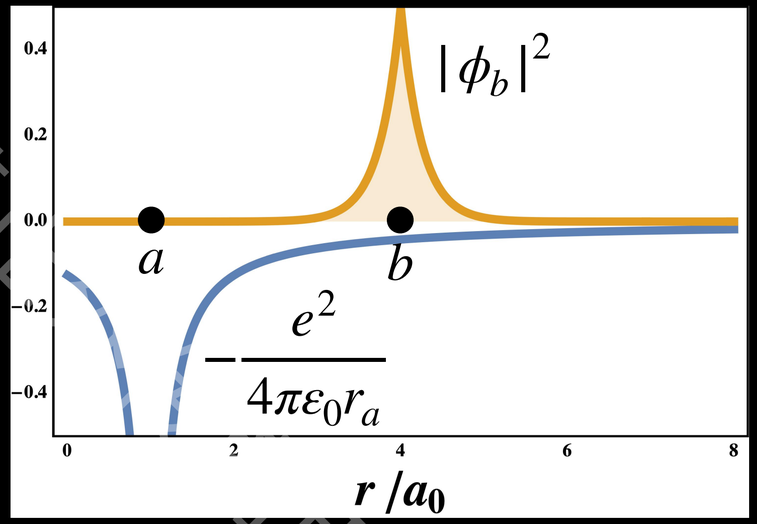
$$= \int\int \underbrace{\phi_a^*\phi_b^*}_{\phi_a^*(\boldsymbol{r}_1)\phi_b^*(\boldsymbol{r}_2)} \left[2E^0 - \frac{e^2}{4\pi\varepsilon_0 r_{b_1}} - \frac{e^2}{4\pi\varepsilon_0 r_{a_2}} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \right] \phi_a\phi_b \mathrm{d}^3 r_1 \mathrm{d}^3 r_2$$

$$\int \phi_a^*(\boldsymbol{r}_1)\left[-\frac{e^2}{4\pi\varepsilon_0 r_{b_1}}\right]\phi_a(\boldsymbol{r}_1)\mathrm{d}^3 r_1 = C = \int \phi_b^*(\boldsymbol{r}_2)\left[-\frac{e^2}{4\pi\varepsilon_0 r_{a_2}}\right]\phi_b(\boldsymbol{r}_2)\mathrm{d}^3 r_2$$

Coulomb interaction energy of nucleus *b* with electron 1 in state *a*.



Coulomb interaction energy of nucleus *a* with electron 2 in state *b*.



$$\langle ab|\frac{e^2}{4\pi\varepsilon_0 R_{ab}}|ab\rangle = E_{\mathrm{RN}}$$

$$\langle ab|\frac{e^2}{4\pi\varepsilon_0 r_{12}}|ab\rangle = E_{\mathrm{CE}}$$

$$E_{\mathrm{part\,1}} = 2E_0 + 2C + E_{\mathrm{RN}} + E_{\mathrm{CE}}$$

$$\langle ab|\hat{H}|ba\rangle$$

$$= \iint \phi_a^* \phi_b^* \left[2E^0 - \frac{e^2}{4\pi\varepsilon_0 r_{b_1}} - \frac{e^2}{4\pi\varepsilon_0 r_{a_2}} + \frac{e^2}{4\pi\varepsilon_0 R_{ab}} + \frac{e^2}{4\pi\varepsilon_0 r_{12}} \right] \phi_b \phi_a \mathrm{d}^3 r_1 \mathrm{d}^3 r_2$$

$$\iint \phi_a^* \phi_b^* 2E^0 \phi_b \phi_a \mathrm{d}^3 r_1 \mathrm{d}^3 r_2 = 2E^0 S$$

$$\langle a| \frac{-e^2}{4\pi\varepsilon_0 r_{b1}} |b\rangle\langle b|a\rangle = DS$$

$$\langle a|b\rangle\langle b| \frac{-e^2}{4\pi\varepsilon_0 r_{a2}} |a\rangle = DS$$

$$\langle ab| \frac{e^2}{4\pi\varepsilon_0 R_{ab}} |ba\rangle = E_{\mathrm{RN}} S^2$$

$$\langle ab| \frac{e^2}{4\pi\varepsilon_0 r_{12}} |ba\rangle = E_{\mathrm{CE}}$$

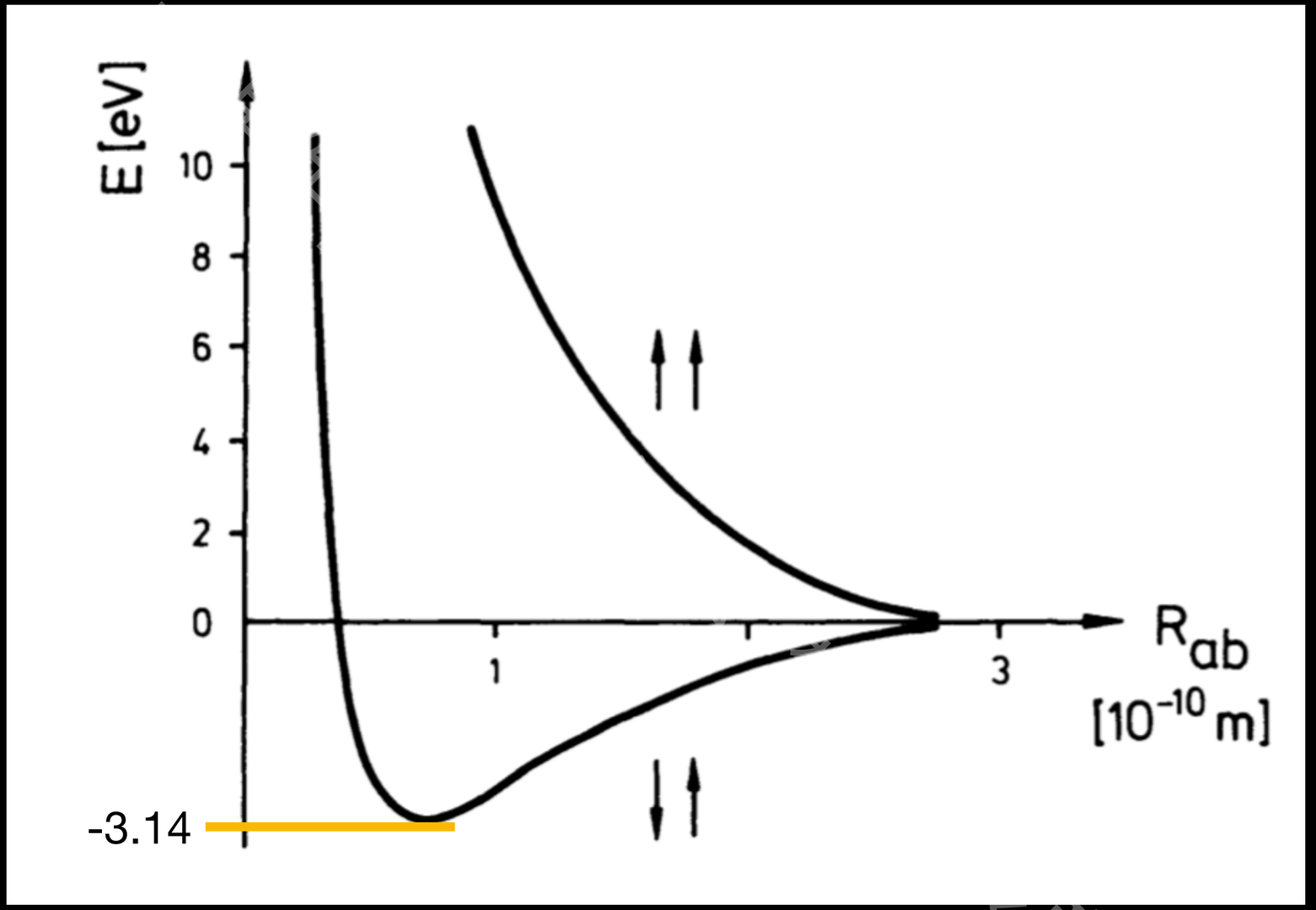
$$E_{\text{part 1}} = 2E_0 + 2C + E_{\text{RI}} + E_{\text{RN}}$$

$$E_{\text{part 2}} = 2E_0S^2 + 2DS + E_{\text{RN}}S^2 + E_{\text{CE}}$$

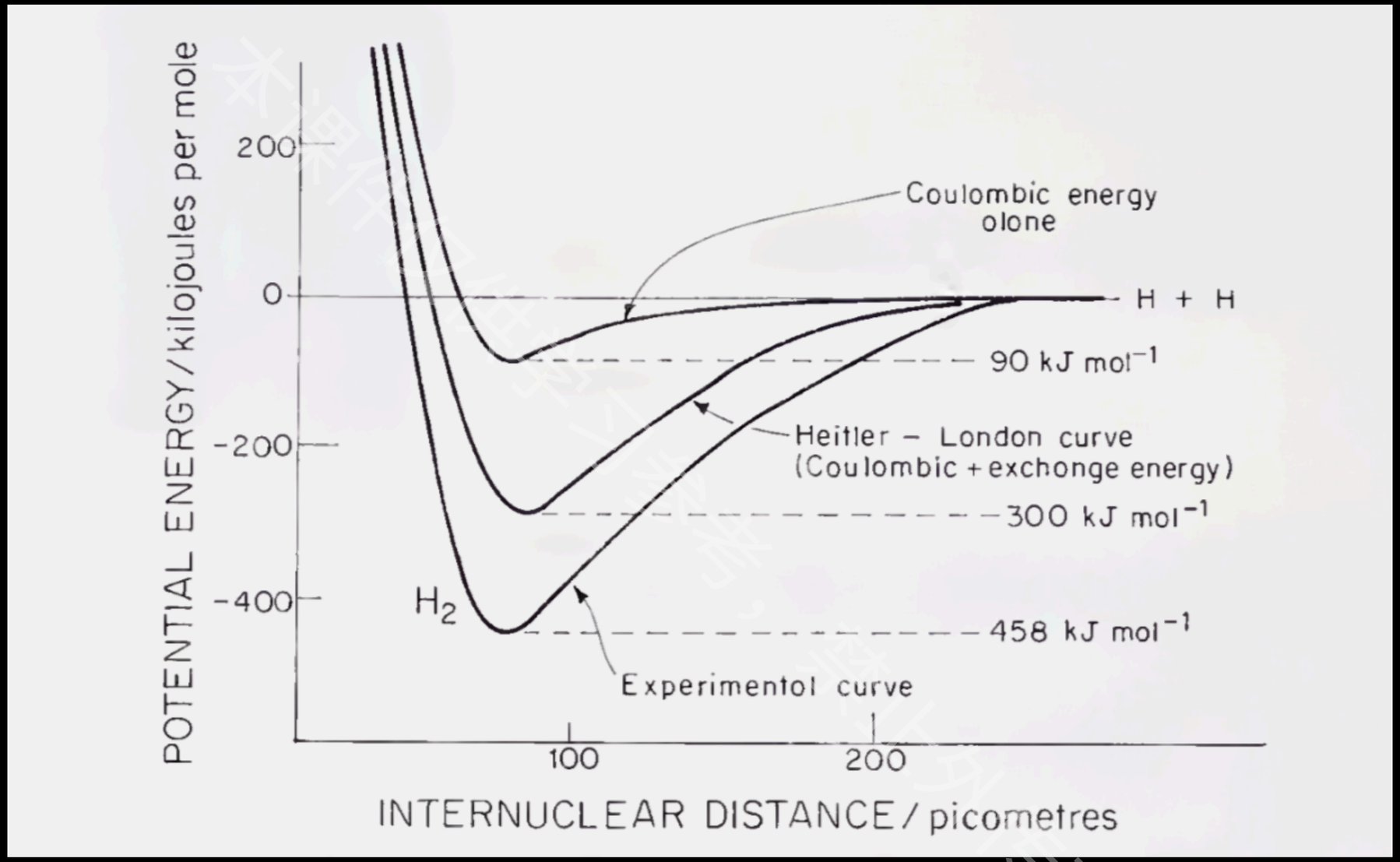
$$E_{g,u} = \frac{\langle \Psi_{g \text{ or } u} | \hat{H} | \Psi_{g \text{ or } u} \rangle}{\langle \Psi | \Psi \rangle} = \frac{2\langle ab | \hat{H} | ab \rangle}{2(1 \pm S^2)} \pm \frac{2\langle ab | \hat{H} | ba \rangle}{2(1 \pm S^2)}$$

$$= \frac{E_{\text{part 1}} \pm E_{\text{part 2}}}{1 \pm S^2}$$

$$= 2E^0 + \frac{2C + E_{\text{RI}}}{1 \pm S^2} \pm \frac{2DS + E_{\text{CE}}}{1 \pm S^2} + E_{\text{RN}}$$



Experimental value: -4.48 eV



Actually, the *exchange* interaction is the driving force of bonding!

Keith Ladler, *The World of Physical Chemistry*, Oxford University Press, 1995

Covalent-Ion resonance

Till now, what wave function we used is one electron move near one atom, and another electron move near another atom separately.

$$\psi_{\mathrm{cov}} = N\left[\phi_a(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2) \pm \phi_b(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2)\right]$$

But still there is some possibility the electrons all reside one single nucleus. And we can assume the final wave function is the linear combination of both.

$$\psi_{\mathrm{ion}} = N'\left[\phi_a(\boldsymbol{r}_1)\phi_a(\boldsymbol{r}_2) \pm \phi_b(\boldsymbol{r}_1)\phi_b(\boldsymbol{r}_2)\right]$$

$$\Psi = \psi_{\mathrm{cov}} + c\psi_{\mathrm{ion}}$$

Influence in Condensed Matter Physics

Resonating VB

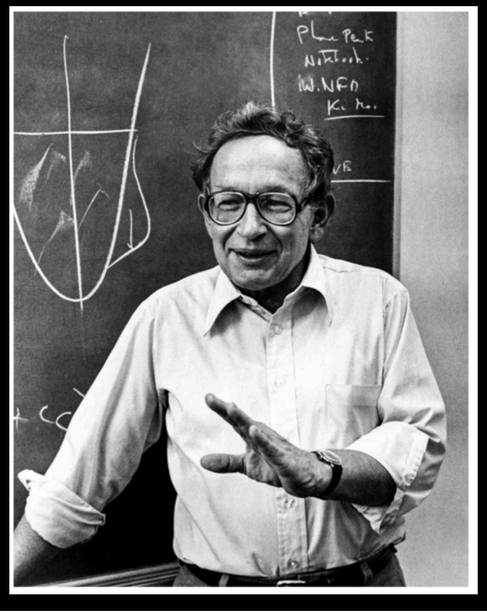
ELSEVIER

Materials Research Bulletin

Volume 8, Issue 2, February 1973, Pages 153-160

Resonating valence bonds: A new kind of insulator? ☆

P.W. Anderson [a, b]



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Hund-Mulliken-Bloch method

One at first ignores the fact that two electrons are present. Instead, we consider the motion of a *single electron in the field of the two nuclei* or, in other words, we begin with the solution of the hydrogen molecule-ion problem.

$$\psi_g(\boldsymbol{r}) = N\left[\phi_a(\boldsymbol{r}) + \phi_b(\boldsymbol{r})\right] \qquad \Psi(\boldsymbol{x}_1, \boldsymbol{x}_2) = \psi_g(\boldsymbol{r}_1)\psi_g(\boldsymbol{r}_2)\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]$$

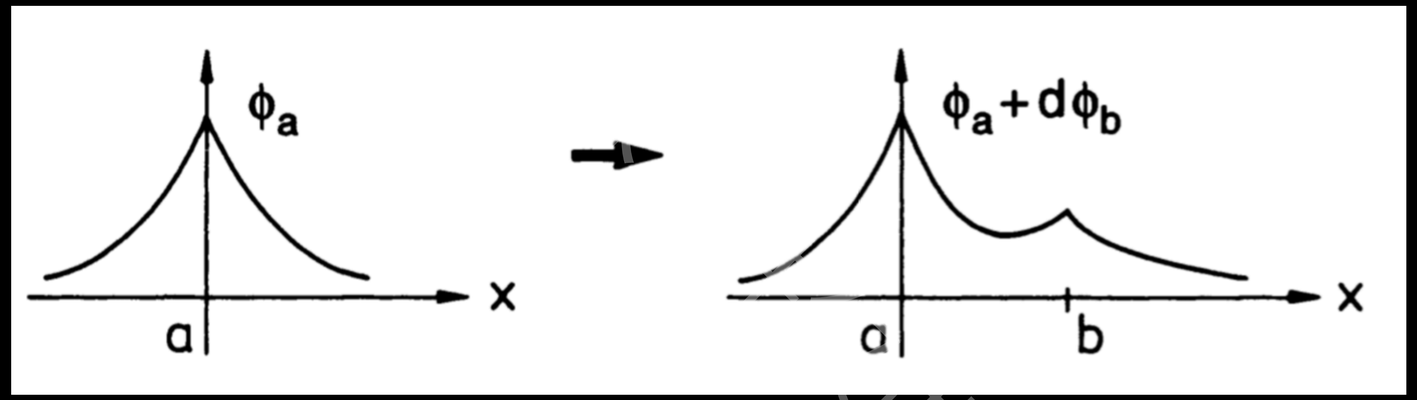
The energy from Hund-Mullikan-Bloch method is higher than that from Heitler-London's, but it's a starting point of calculating multi-electron molecules. This is the thought of *LCAO*: Linear Combination of Atomic Orbital.

Outlines of MO

In this type of theory, the A and B atoms are brought together firstly to become a ‘united atom’ AB. Then the electrons are fed one by one into the AB molecule.

This thought is firstly given by Sir John Edward Lennard-Jones (1894-1954). The MO method is proposed to explain molecular spectra.

The contributors including Sir Lennard-Jones, Hund, Mullikan, Gerhard Herzberg, Felix Bloch (extended this thought into investigations of solids), Charles A. Coulson, Erick/Walter Hückel (they are brothers) and so on.



$$\phi_a \to \phi_a + d\phi_b$$
$$\phi_b \to \phi_b + d\phi_a$$

$$\Psi_g(\boldsymbol{r}_1, \boldsymbol{r}_2) = \left[\phi_a(\boldsymbol{r}_1) + d\phi_b(\boldsymbol{r}_1)\right]\left[\phi_b(\boldsymbol{r}_2) + d\phi_a(\boldsymbol{r}_2)\right] + \left[\phi_b(\boldsymbol{r}_1) + d\phi_a(\boldsymbol{r}_1)\right]\left[\phi_a(\boldsymbol{r}_2) + d\phi_b(\boldsymbol{r}_2)\right]$$
$$= (1 + d^2)\left[|ab\rangle + |ba\rangle\right] + 2d\left[|aa\rangle + |bb\rangle\right]$$
$$\propto \psi_{\text{cov}} + c\psi_{\text{ion}}$$

$$c = \frac{2d}{1 + d^2}$$

$$\hat{H} = \overbrace{\sum_{i=1}^{K\ \text{nuclei}} -\frac{\hbar^2}{2m_i}\nabla^2_{\mathbf{r}_i} + \sum_{j=1}^{N\ \text{electrons}} -\frac{\hbar^2}{2m_i}\nabla^2_{\mathbf{r}_j}}^{\text{Kinetic energy (nucl. and el.)}} + \overbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{k=1}^{N}\sum_{l>k}^{N}\frac{e^2}{|\mathbf{r}_k - \mathbf{r}_l|}}^{\text{Coulomb repulsion (el.-el.)}}$$
$$\underbrace{-\frac{1}{4\pi\epsilon_0}\sum_{m=1}^{K}\sum_{n=1}^{N}\frac{Z_m e^2}{|\mathbf{r}_n - \mathbf{R}_m|}}_{\text{Coulomb attraction (el.-nucl.)}} + \underbrace{\frac{1}{4\pi\epsilon_0}\frac{1}{2}\sum_{o=1}^{K}\sum_{p>0}^{K}\frac{Z_o Z_p e^2}{|\mathbf{R}_o - \mathbf{R}_k|}}_{\text{Coulomb repulsion (nucl.-nucl.)}} \qquad (2)$$

Multi-electron molecules: H-F

General method

Preliminary

Setup

There are N electrons:

$$\boldsymbol{r}_j, \quad j = 1,2,\cdots,N$$

There are M nuclei:

$$\boldsymbol{R}_K, Z_K, \quad K = 1,2,\cdots,M$$

$$V(\boldsymbol{r}_j) = \sum_K V_K(\boldsymbol{r}_j)$$

$$V_K(\boldsymbol{r}_j) = -\frac{Z_K e^2}{4\pi\varepsilon_0 |\boldsymbol{R}_K - \boldsymbol{r}_j|}$$

$$|\boldsymbol{R}_K - \boldsymbol{r}_j| = \sqrt{(X_K - x_j)^2 + (Y_K - y_j)^2 + (Z_K - z_j)^2}$$

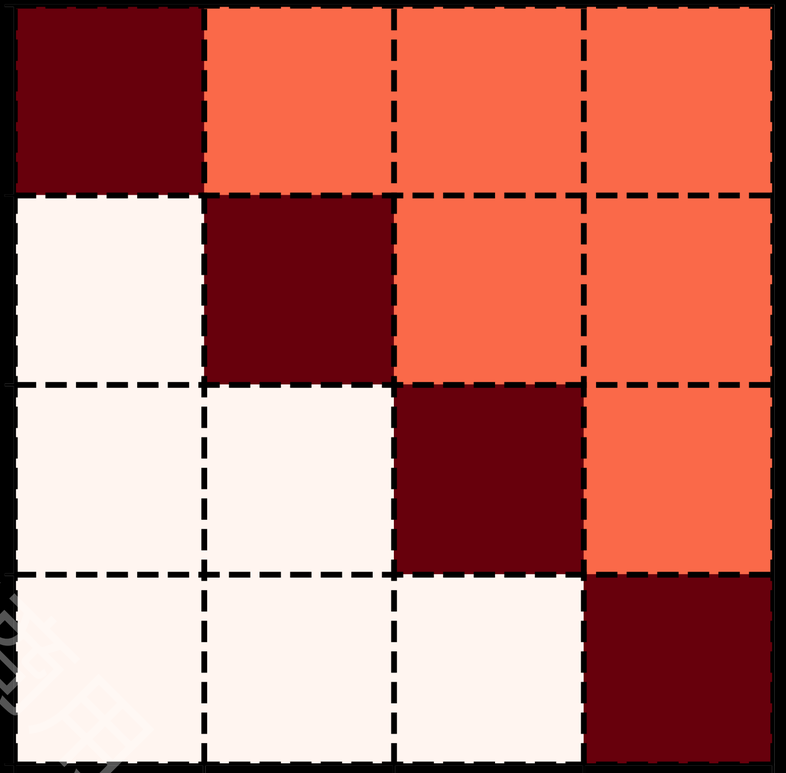
Hamiltonian

$$\hat{H}(\boldsymbol{r}_j) \equiv \hat{H}(j) = \frac{\hbar^2}{2m_0}\nabla_j^2 + V(\boldsymbol{r}_j)$$

Here we have neglected the spin-orbit interaction.

$$W_{jl} = \frac{e^2}{4\pi\varepsilon_0 |\boldsymbol{r}_j - \boldsymbol{r}_l|} \qquad \hat{H}_{\text{int}} = \frac{1}{2}\sum_{j\neq l} W_{jl} = \sum_{j<l} W_{jl}$$

$$\hat{H} = \sum_j \hat{H}(j) + \hat{H}_{\text{int}}$$



Things must consider:

1. Pauli exclusion principle.
2. Electrons interact each other.

Distraction: Linear Variational Principle

From previous discussion on variational principle, there is no *a priori* choice of the trial basis: $|\tilde{\Phi}\rangle$. So we need a systematical guess for it.

$$|\tilde{\Phi}\rangle = \sum_{i=1}^{N} c_i |\Psi_i\rangle$$

Known basis

Setup:

$$\langle \Psi_i | \Psi_j \rangle = \delta_{ij} \quad \langle \Psi_i | \hat{H} | \Psi_j \rangle = H_{ij} \quad \langle \tilde{\Phi} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j \langle \Psi_i | \Psi_j \rangle = \sum_i c_i^2 = 1$$

In general, this is a real number

$$\langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j H_{ij}$$

Lagrange multiplier

Goal: optimize this summation:

$$\langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j H_{ij}$$

Restraint: orthonormalization

$$\langle \tilde{\Phi} | \tilde{\Phi} \rangle = \sum_{ij} c_i c_j \langle \Psi_i | \Psi_j \rangle = \sum_i c_i^2 = 1$$

$$\mathscr{L} = \langle \tilde{\Phi} | \hat{H} | \tilde{\Phi} \rangle - E(\langle \tilde{\Phi} | \tilde{\Phi} \rangle - 1) = \sum_{ij} c_i c_j H_{ij} - \tilde{E}(\sum_i c_i^2 - 1)$$

$$\frac{\partial}{\partial c_k} \mathscr{L} = 0, \quad k = 1,2,\cdots,N$$

$$\sum_j c_j H_{ij} - \tilde{E} c_i = 0$$

$$\sum_j c_j H_{ij} - \tilde{E} c_i = 0$$

Linear variational equation: $\boldsymbol{Hc} = \tilde{E}\boldsymbol{c}$

$\boldsymbol{Hc}^{\alpha} = \tilde{E}_{\alpha}\boldsymbol{c}^{\alpha} \quad \alpha = 0,1,\cdots,N-1$

Introduce $\boldsymbol{C}$: $C_{i\alpha} = c_i^{\alpha}$

$$\boldsymbol{HC} = \boldsymbol{C}\tilde{\boldsymbol{E}}$$

$$\tilde{E}_0 = \langle \tilde{\Phi}_0 | \hat{H} | \tilde{\Phi}_0 \rangle \geq E_0$$

Atomic Units

Physical quantity	Conversion factor X	Value of X (SI)
Length	a_0	5.2918×10^{-11} m
Mass	m_e	9.1095×10^{-31} kg
Charge	e	1.6022×10^{-19} C
Energy	$\mathscr{E}_a$	4.3598×10^{-18} J
Angular momentum	$\hbar$	1.0546×10^{-34} J s
Electric dipole moment	ea_0	8.4784×10^{-30} Cm
Electric polarizability	$e^2a_0^2\mathscr{E}_a^{-1}$	1.6488×10^{-41} $C^2m^2J^{-1}$
Electric field	$\mathscr{E}_a e^{-1} a_0^{-1}$	5.1423×10^{11} V m^{-1}
Wave function	$a_0^{-3/2}$	2.5978×10^{15} $m^{-3/2}$

Attila Szabo & Neil Ostlund, *Modern Quantum Chemistry*, Dover, 1996

Many electron Hamiltonian in a.u.

$$\hat{H} = -\sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M} \frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}}$$

Spin Orbitals and Spatial Orbitals

Orbital	A wave function for a single particle, such as electron.
Molecular Orbital	A wave function of a electron in a molecule.
Spatial Orbital	A function of the position vector and describes the distribution density as its square norm.
Spin Orbital	Spatial orbital multiplies a spin function, either spin-up or spin-down.

In quantum mechanics one replaces the word 'orbit' with *orbital*, a word introduced by R. S. Mulliken who defined it in a simple way by saying that an orbital is as much like an orbit as quantum mechanics permits. More precisely, the word 'orbital' refers to a wavefunction that relates to a single electron associated with an atom or molecule.

Keith Ladler, *The World of Physical Chemistry*, Oxford University Press, 1995

$$\int \psi_i^*(\boldsymbol{r})\psi_j(\boldsymbol{r})\mathrm{d}^3 r = \delta_{ij} \equiv \langle i|j\rangle$$

Spatial orbital

$$\chi(\boldsymbol{x}) = \begin{cases} \psi(\boldsymbol{r})\alpha(\omega) \\ \text{or} \\ \psi(\boldsymbol{r})\beta(\omega) \end{cases}$$

Spin orbital

Given K spatial orbitals $\{\psi_i | i = 1,2,\cdots,K\}$, one can form a set of $2K$ spin orbitals $\{\chi_i | i = 1,2,\cdots,2K\}$ as:

$$\left.\begin{aligned} \chi_{2i-1}(\boldsymbol{x}) &= \psi_i(\boldsymbol{r})\alpha(\omega) \\ \chi_{2i}(\boldsymbol{x}) &= \psi_i(\boldsymbol{r})\beta(\omega) \end{aligned}\right\} i = 1,2,\cdots,K$$

$$\langle \chi_i | \chi_j \rangle \equiv \int \chi_i^*(\boldsymbol{x})\chi_j(\boldsymbol{x})\mathrm{d}\boldsymbol{x} = \delta_{ij}$$

Hartree Product

$$\hat{H} = \sum_i \hat{H}(i) \qquad \hat{H}(i)\chi_j(\boldsymbol{x}_i) = \varepsilon_j \chi_j(\boldsymbol{x}_i)$$

$$\Psi^{\mathrm{HP}}(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) = \chi_i(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)\cdots\chi_k(\boldsymbol{x}_N)$$

$$\hat{H}\Psi^{\mathrm{HP}} = E\Psi^{\mathrm{HP}} \qquad E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k$$

Slater Determinant for many electron system

Recall the Slater determinant for H_2:

$$\Psi \propto \begin{vmatrix} \phi_a(\boldsymbol{r}_1)\alpha(1) & \phi_a(\boldsymbol{r}_2)\alpha(2) \\ \phi_b(\boldsymbol{r}_1)\alpha(1) & \phi_b(\boldsymbol{r}_2)\alpha(2) \end{vmatrix}$$

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \cdots & \chi_k(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \cdots & \chi_k(\boldsymbol{x}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \cdots & \chi_k(\boldsymbol{x}_N) \end{vmatrix}$$

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \cdots & \chi_k(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \cdots & \chi_k(\boldsymbol{x}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \cdots & \chi_k(\boldsymbol{x}_N) \end{vmatrix}$$

To learn second quantization from zero, one can resort to C. Kittel, *Quantum Theory of Solids*, 2nd edition, 1987, Chapter 5.

$$= |\chi_i(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)\cdots\chi_k(\boldsymbol{x}_N)\rangle$$

$$= |\chi_i\chi_j\cdots\chi_k\rangle = |ij\cdots k\rangle$$

$$= \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots \hat{a}_k^\dagger |00\cdots0\rangle$$

$$\left\{ \hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger \right\} = 0$$

$$|\cdots\chi_m\cdots\chi_n\cdots\rangle = -|\cdots\chi_n\cdots\chi_m\cdots\rangle$$

$$|\cdots\chi_m\cdots\chi_n\cdots\rangle = \hat{a}_m^\dagger \hat{a}_n^\dagger |\cdots0\cdots0\cdots\rangle = -\hat{a}_n^\dagger \hat{a}_m^\dagger |\cdots0\cdots0\cdots\rangle = -|\cdots\chi_n\cdots\chi_m\cdots\rangle$$

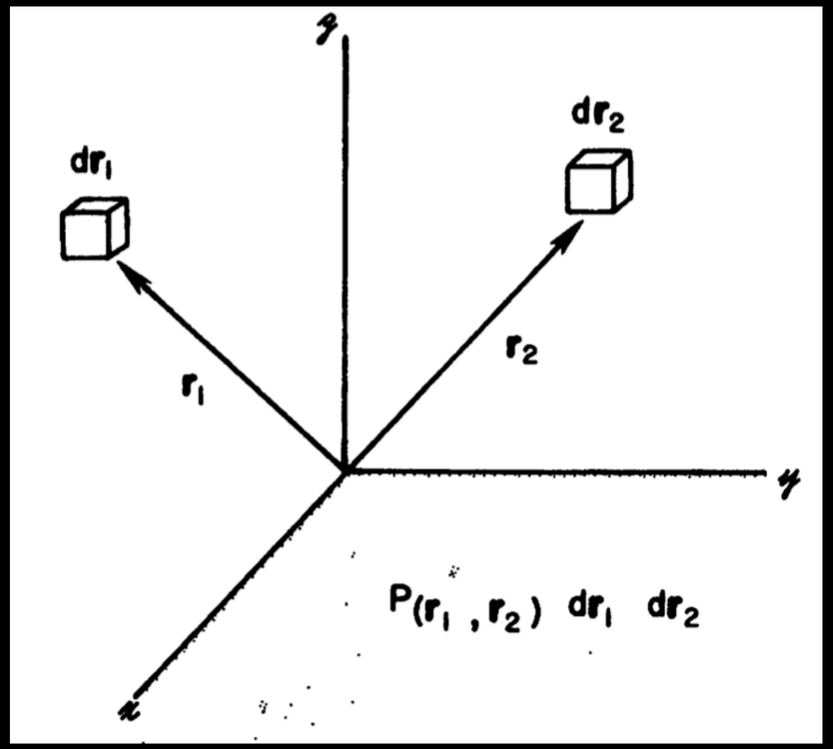
$$|K\rangle = |ij\rangle$$
$$|L\rangle = |kl\rangle$$

$$\langle K|L\rangle = \frac{1}{\sqrt{2!}}\frac{1}{\sqrt{2!}}(\langle ij| - \langle ji|)(|kl\rangle - |lk\rangle)$$

$$= \frac{1}{2}(\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk} - \delta_{jk}\delta_{il} + \delta_{jl}\delta_{ik})$$

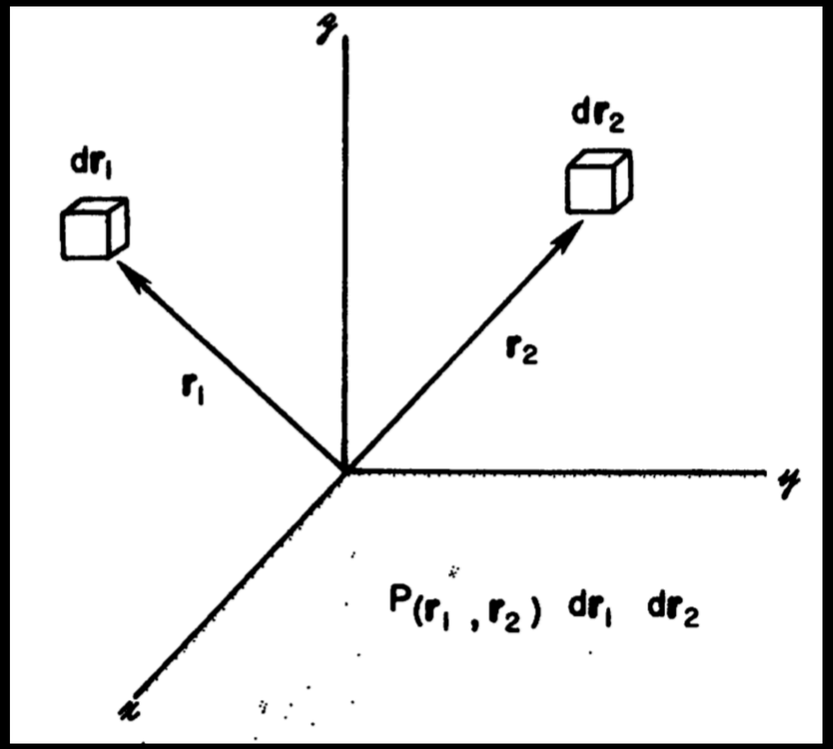
$$= \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}$$

$$|\Psi\rangle = |12\rangle$$
$$= |\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\rangle$$
$$= |\psi_1(\boldsymbol{r}_1)\sigma(\omega_1)\psi_2(\boldsymbol{r}_2)\sigma(\omega_2)\rangle$$
$$= \hat{a}_1^\dagger \hat{a}_2^\dagger |0\rangle$$



$$\langle 12|12\rangle = \int\int\int\int \psi_1^*(\boldsymbol{r}_1)\sigma_1^*(\omega_1)\psi_2^*(\boldsymbol{r}_2)\sigma_2^*(\omega_2) \times$$
$$\psi_1(\boldsymbol{r}_1)\sigma_1(\omega_1)\psi_2(\boldsymbol{r}_2)\sigma_2(\omega_2)\mathrm{d}^3r_1\mathrm{d}^3r_2\mathrm{d}\omega_1\mathrm{d}\omega_2$$

$$|\Psi\rangle = |12\rangle$$
$$= |\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2)\rangle$$
$$= |\psi_1(\boldsymbol{r}_1)\sigma(\omega_1)\psi_2(\boldsymbol{r}_2)\sigma(\omega_2)\rangle$$
$$= \hat{a}_1^\dagger \hat{a}_2^\dagger$$



Suppose:

$$\sigma_1(\omega) = \alpha(\omega),\ \sigma_2(\omega) = \beta(\omega)$$

$$\langle\Psi|\Psi\rangle = \langle 12|12\rangle$$
$$= \frac{1}{2}(\langle 12| - \langle 21|)(|12\rangle - |21\rangle)$$
$$= \frac{1}{2}(1 - 0 - 0 + 1) = 1$$

$$\langle 12|12\rangle = \int\int\int\int \psi_1^*(\boldsymbol{r}_1)\sigma_1^*(\omega_1)\psi_2^*(\boldsymbol{r}_2)\sigma_2^*(\omega_2) \times$$
$$\psi_1(\boldsymbol{r}_1)\sigma_1(\omega_1)\psi_2(\boldsymbol{r}_2)\sigma_2(\omega_2)\mathrm{d}^3r_1\mathrm{d}^3r_2\mathrm{d}\omega_1\mathrm{d}\omega_2$$

If use Wick's theorem, the deduction can become easier.

$$\langle \Psi | \Psi \rangle = \langle 12 | 12 \rangle$$

$$= \frac{1}{2}(\langle 12| - \langle 21|)(|12\rangle - |21\rangle)$$

$$= \frac{1}{2}\langle 0|(\hat{a}_2\hat{a}_1 - \hat{a}_1\hat{a}_2)(\hat{a}_1^\dagger\hat{a}_2^\dagger - \hat{a}_2^\dagger\hat{a}_1^\dagger)|0\rangle$$

$$= \frac{1}{2}\langle 0|(\hat{a}_2\hat{a}_1\hat{a}_1^\dagger\hat{a}_2^\dagger - \hat{a}_2\hat{a}_1\hat{a}_2^\dagger\hat{a}_1^\dagger -$$

$$\hat{a}_1\hat{a}_2\hat{a}_1^\dagger\hat{a}_2^\dagger + \hat{a}_1\hat{a}_2\hat{a}_2^\dagger\hat{a}_1^\dagger)|0\rangle$$

$$= \frac{1}{2} \times 2 = 1$$

Second Quantization Representation

Another notation formula saving life

$$\left\{\hat{a}_\alpha^\dagger, \hat{a}_\beta^\dagger\right\} \equiv \hat{a}_\alpha^\dagger \hat{a}_\beta^\dagger + \hat{a}_\beta^\dagger \hat{a}_\alpha^\dagger = 0$$

$$\left\{\hat{a}_\alpha, \hat{a}_\beta\right\} = 0$$

$$\left\{\hat{a}_\alpha, \hat{a}_\beta^\dagger\right\} = \delta_{\alpha\beta}$$

$$\hat{n}_i = \hat{a}_i^\dagger \hat{a}_i$$

$$|n_1, n_2, \cdots, n_i, \cdots, \rangle$$

$$= \frac{(\hat{a}_1^\dagger)^{n_1}}{\sqrt{(n_1)!}} \frac{(\hat{a}_2^\dagger)^{n_2}}{\sqrt{(n_2)!}} \cdots \frac{(\hat{a}_i^\dagger)^{n_i}}{\sqrt{(n_i)!}} \cdots |0\rangle$$

$$= \prod_{j=1}^{N} \frac{(\hat{a}_j^\dagger)^{n_j}}{\sqrt{(n_j)!}} |0\rangle$$

$$\hat{n}_i |n_1, n_2, \cdots, n_i, \cdots, \rangle$$

$$= n_i |n_1, n_2, \cdots, n_i, \cdots, \rangle$$

$$\hat{a}_i|n_1,n_2,\cdots,n_i,\cdots\rangle$$

$$=\frac{1}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}}\hat{a}_i(\hat{a}_1^\dagger)^{n_1}(\hat{a}_2^\dagger)^{n_2}\cdots(\hat{a}_i^\dagger)^{n_i}\cdots|0\rangle$$

$$=\frac{(-1)^{n_1}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}}(\hat{a}_1^\dagger)^{n_1}\hat{a}_i(\hat{a}_2^\dagger)^{n_2}\cdots(\hat{a}_i^\dagger)^{n_i}\cdots|0\rangle$$

$$=\frac{(-1)^{\sum_{j=1}^{i-1}n_j}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}}(\hat{a}_1^\dagger)^{n_1}(\hat{a}_2^\dagger)^{n_2}\cdots\hat{a}_i(\hat{a}_i^\dagger)^{n_i}\cdots|0\rangle$$

$$=\frac{\sigma_i}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}}(\hat{a}_1^\dagger)^{n_1}(\hat{a}_2^\dagger)^{n_2}\cdots(1-\hat{a}_i^\dagger\hat{a}_i)(\hat{a}_i^\dagger)^{n_i-1}\cdots|0\rangle$$

$$=\sigma_i(1-n_i)|n_1,n_2,\cdots,(n_i-1),\cdots\rangle$$

$$\left\{\hat{a}_\alpha,\hat{a}_\beta^\dagger\right\}\Big|_{\alpha\neq\beta}=\hat{a}_\alpha\hat{a}_\beta^\dagger+\hat{a}_\beta^\dagger\hat{a}_\alpha=0$$

$$\left\{\hat{a}_\alpha,\hat{a}_\alpha^\dagger\right\}=\hat{a}_\alpha\hat{a}_\alpha^\dagger+\hat{a}_\alpha^\dagger\hat{a}_\alpha=1$$

$$\sigma_i=(-1)^{\sum_{j=1}^{i-1}n_j}$$

$$\begin{cases}=0, & n_i=0\\ =\sigma_i|n_1,n_2,\cdots,0_i,\cdots\rangle, & n_i=1\end{cases}$$

$$\hat{a}_i^\dagger \left| n_1, n_2, \cdots, n_i, \cdots \right\rangle$$

$$= \frac{1}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} \hat{a}_i^\dagger (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_i^\dagger)^{n_i} \cdots \left| 0 \right\rangle$$

$$= \frac{(-1)^{n_1}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} (\hat{a}_1^\dagger)^{n_1} \hat{a}_i^\dagger (\hat{a}_2^\dagger)^{n_2} \cdots (\hat{a}_i^\dagger)^{n_i} \cdots \left| 0 \right\rangle$$

$$= \frac{(-1)^{\sum_{j=1}^{i-1} n_j}}{\sqrt{(n_1)!(n_2)!\cdots(n_i)!\cdots}} (\hat{a}_1^\dagger)^{n_1} (\hat{a}_2^\dagger)^{n_2} \cdots \hat{a}_i^\dagger (\hat{a}_i^\dagger)^{n_i} \cdots \left| 0 \right\rangle$$

$$\sigma_i = (-1)^{\sum_{j=1}^{i-1} n_j}$$

$$\hat{a}_i^\dagger \left| n_i \right\rangle = \sqrt{n_i + 1} \left| n_i + 1 \right\rangle$$

$$= \sigma_i \sqrt{n_i + 1} \left| n_1, n_2, \cdots, n_i + 1, \cdots \right\rangle$$

$$\begin{cases} = \sigma_i \left| n_1, n_2, \cdots, 1_i, \cdots \right\rangle, & n_i = 0 \\ = 0, & n_i = 1 \end{cases}$$

$$\Psi(\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(\boldsymbol{x}_1) & \chi_j(\boldsymbol{x}_1) & \cdots & \chi_k(\boldsymbol{x}_1) \\ \chi_i(\boldsymbol{x}_2) & \chi_j(\boldsymbol{x}_2) & \cdots & \chi_k(\boldsymbol{x}_2) \\ \vdots & \vdots & \cdots & \vdots \\ \chi_i(\boldsymbol{x}_N) & \chi_j(\boldsymbol{x}_N) & \cdots & \chi_k(\boldsymbol{x}_N) \end{vmatrix}$$

$$= |\chi_i(\boldsymbol{x}_1)\chi_j(\boldsymbol{x}_2)\cdots\chi_k(\boldsymbol{x}_N)\rangle$$

$$= |\chi_i\chi_j\cdots\chi_k\rangle = |ij\cdots k\rangle$$

$$= \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots \hat{a}_k^\dagger |00\cdots 0\rangle$$

$$= \hat{a}_i^\dagger \hat{a}_j^\dagger \cdots \hat{a}_k^\dagger |0\rangle \qquad n_i = 1$$

In ground state calculations, all the shown positions are single-occupied.
So there is slight difference from the general case.

Second quantization of operators

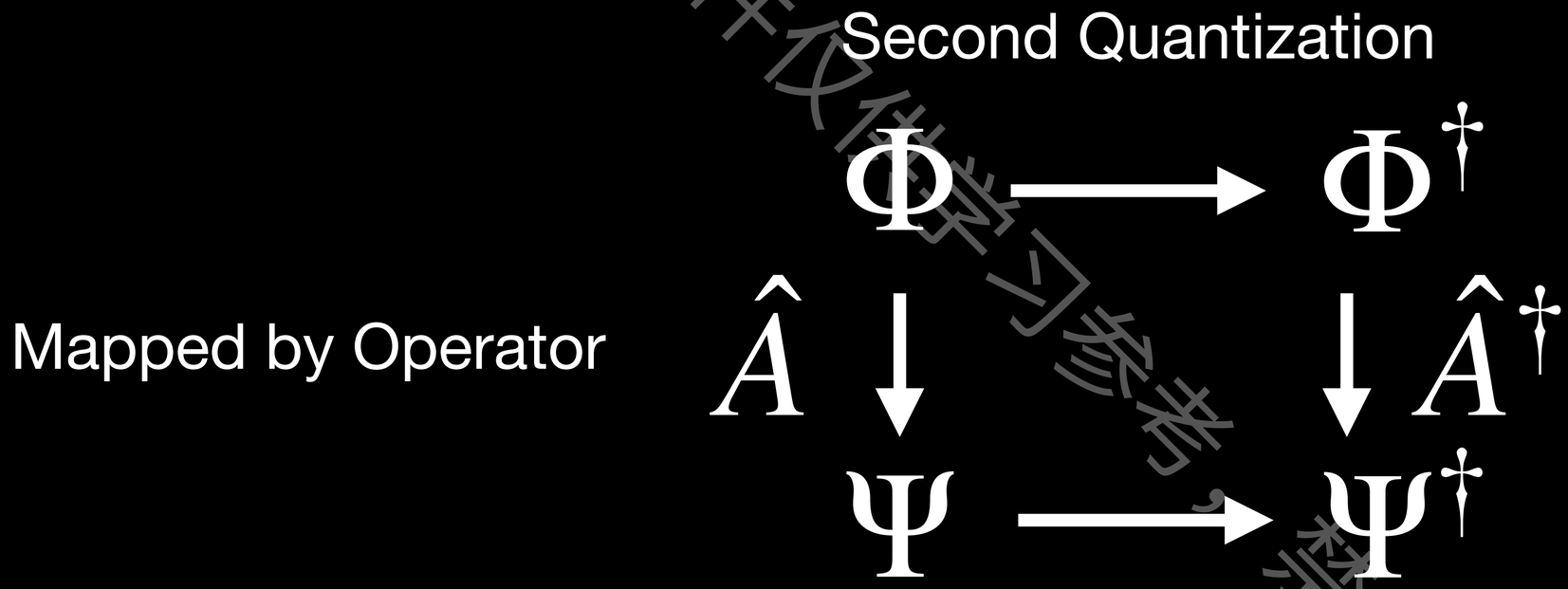


Table 3.1 First and second quantization treatment of conserved particles.

	First quantization	Second quantization
Wavefunction $\longrightarrow$ field operator	$\psi(x) = \langle x\|\psi\rangle$	$\hat{\psi}(x)$
Commutator	$[x, p] = i\hbar$	$[\hat{\psi}(x), \hat{\psi}^\dagger(x')]_\mp = \delta^D(x - x')$
Density	$\rho(x) = \|\psi(x)\|^2$	$\hat{\rho}(x) = \hat{\psi}^\dagger(x)\hat{\psi}(x)$
Arbitrary basis	$\psi_\lambda = \langle\lambda\|\psi\rangle$	$\hat{\psi}_\lambda$
Change of basis	$\langle\tilde{s}\|\psi\rangle = \sum_\lambda \langle\tilde{s}\|\lambda\rangle\langle\lambda\|\psi\rangle$	$\hat{a}_s = \sum_\lambda \langle\tilde{s}\|\lambda\rangle\hat{\psi}_\lambda$
Orthogonality	$\langle\lambda\|\lambda'\rangle = \delta_{\lambda\lambda'}$	$[\psi_\lambda, \psi^\dagger_{\lambda'}]_\mp = \delta_{\lambda\lambda'}$
One-particle energy	$\frac{p^2}{2m} + U$	$\int_x \hat{\psi}^\dagger(x)\left(-\frac{\hbar^2}{2m} + U(x)\right)\hat{\psi}(x)$
Interaction	$\sum_{i<j} V(x_i - x_j)$	$\hat{V} = \frac{1}{2}\int_{x,x'} V(x - x') : \hat{\rho}(x)\hat{\rho}(x') : = \frac{1}{2}\sum V(\mathbf{q}) c^\dagger_{\mathbf{k}+\mathbf{q}} c^\dagger_{\mathbf{k}'-\mathbf{q}} c_{\mathbf{k}'} c_{\mathbf{k}}$
Many-body wavefunction	$\Psi(x_1, x_2, \ldots x_N)$	$\langle 0\|\hat{\psi}(x_1)\cdots\hat{\psi}(x_N)\|\Psi\rangle$
Schrödinger equation	$\left(\sum \mathcal{H}_i + \sum_{i<j} V_{ij}\right)\Psi = i\hbar\dot{\Psi}$	$\left[\mathcal{H}^{(0)} + \int_{x'} \hat{\rho}(x')V(x' - x)\right]\hat{\psi}(x) = i\hbar\dot{\psi}(x)$

Piers Coleman, *Introduction to Many-Body Physics*, 2015

Single-particle operator

First, we consider single electron case.

$$\hat{A}\phi_i = \psi_i$$

$$\psi_i = \sum_k C_{ik}\phi_k$$

$$\hat{A}\phi_i = \sum_k C_{ik}\phi_k$$

$$\langle \phi_l | \hat{A} | \phi_i \rangle = \sum_k C_{ik}\langle \phi_l | \phi_k \rangle$$

$$\boxed{A_{li} = C_{il}}$$

Second quantization:

$$\hat{A}^\dagger \phi_i^\dagger |0\rangle = \psi_i^\dagger |0\rangle$$

$$\psi_i^\dagger = \sum_k C_{ik}\phi_k^\dagger$$

$$\hat{A}^\dagger \phi_i^\dagger = \sum_k C_{ik} \phi_k^\dagger$$

$$\hat{A}^\dagger \phi_i^\dagger \phi_i = \sum_k C_{ik} \phi_k^\dagger \phi_i$$

$$\hat{A}^\dagger \sum_i \phi_i^\dagger \phi_i = \sum_{k,i} C_{ik} \phi_k^\dagger \phi_i$$

$$\hat{A}^\dagger \hat{N} = \sum_{k,i} C_{ik} \phi_k^\dagger \phi_i$$

Since there is only 1 electron

$$\hat{A} \longrightarrow \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i$$

$$\hat{A}^\dagger = \sum_{k,i} C_{ik} \phi_k^\dagger \phi_i$$

Insert the relation: $A_{li} = C_{il}$

$$\hat{A}^\dagger = \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i$$

Proof of the second quantization of single electron operator

$$\langle \phi_l | \hat{A} | \phi_l \rangle = A_{ll}$$

$$\langle \phi_l | \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i | \phi_l \rangle$$

$$= \langle 0 | \phi_l \sum_{k,i} A_{ki} \phi_k^\dagger \phi_i \phi_l^\dagger | 0 \rangle = \langle 0 | \sum_{k,i} A_{ki} \phi_l \phi_k^\dagger \phi_i \phi_l^\dagger | 0 \rangle$$

$$= \langle 0 | \sum_{k,i} A_{ki} (\delta_{lk} - \phi_k^\dagger \phi_l)(\delta_{il} - \phi_l^\dagger \phi_i) | 0 \rangle$$

$$= \langle 0 | \sum_{k,i} A_{ki} \delta_{lk} (\delta_{il} - \phi_l^\dagger \phi_i) + \phi_k^\dagger \phi_i (1 - \hat{n}_l) | 0 \rangle$$

$$= \langle 0 | \sum_{k,i} A_{ki} \delta_{lk} \delta_{il} | 0 \rangle = A_{ll}$$

Extend our finding to N-particles

$$\hat{A} = \sum_{n=1}^{N} \hat{A}_n$$

This single-particle operator has lots of examples, such as:

$$\hat{T} = -\frac{1}{2}\sum_n \nabla_n^2 \quad \hat{V} = -\sum_n \left[\sum_A \frac{Z_A}{|\boldsymbol{R}_A - \boldsymbol{r}_n|}\right] \quad \hat{\mu} = \sum_n \hat{\mu}_n$$

$$\Psi = \hat{A}\Phi \longrightarrow \Psi^\dagger = \hat{A}^\dagger \Phi^\dagger$$

$$\Psi^\dagger|0\rangle = \sum_n \hat{A}_n^\dagger \Phi^\dagger |0\rangle$$

$$= \sum_n \hat{A}_n^\dagger \phi_N^\dagger \cdots \phi_n^\dagger \cdots \phi_1^\dagger |0\rangle$$

$$\hat{A}_n^\dagger \phi_n^\dagger = \sum_l C_{nl}\phi_l^\dagger$$

$$= \sum_l A_{ln}\phi_l^\dagger$$

$$\Psi^\dagger|0\rangle = \sum_n \phi_1^\dagger \cdots (\sum_l C_{nl}\phi_l^\dagger) \cdots \phi_N^\dagger |0\rangle$$

$$= \sum_n \sum_l A_{ln}\phi_1^\dagger \cdots \phi_l^\dagger \cdots \phi_N^\dagger |0\rangle$$

$$= \sum_{n,l} A_{ln}\phi_1^\dagger \cdots \phi_l^\dagger (\phi_n \phi_n^\dagger) \cdots \phi_N^\dagger |0\rangle$$

$$= \sum_{n,l} A_{ln}(-1)^{l-1}\phi_l^\dagger (-1)^{l-1}\phi_n \phi_1^\dagger \cdots \phi_n^\dagger \cdots \phi_N^\dagger |0\rangle$$

$$= \sum_{n,l} (A_{ln}\phi_l^\dagger \phi_n)\left[\phi_1^\dagger \cdots \phi_n^\dagger \cdots \phi_N^\dagger |0\rangle\right]$$

$$\hat{A}_n^\dagger \phi_n^\dagger = \sum_l A_{ln}\phi_l^\dagger$$

$$A_{ln} = \langle l|\hat{A}|n\rangle$$

$$\hat{A}_{(\text{single-particle})} \rightarrow \sum_{n,l} A_{ln}\phi_l^\dagger \phi_n$$

Verification of the one-body operator

$$|\Psi_0\rangle = |1\cdots a\cdots b\cdots N\rangle$$

$$\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{\mu\nu}\langle\mu|\hat{h}|\nu\rangle\langle\Psi_0|\hat{a}_\mu^\dagger\hat{a}_\nu|\Psi_0\rangle$$

Here we are considering the ground state, so μ and ν must be within the set $\{1,2,\cdots,a,\cdots,b,\cdots,N\}$:

$$\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{ab}\langle a|\hat{h}|b\rangle\langle\Psi_0|\hat{a}_a^\dagger\hat{a}_b|\Psi_0\rangle$$

$$= \sum_{ab}\langle a|\hat{h}|b\rangle\langle\Psi_0|(\delta_{ab}-\hat{a}_b\hat{a}_a^\dagger)|\Psi_0\rangle$$

Since in the ground state, all $\{1,\cdots,a,\cdots,b,\cdots,N\}$ are occupied, add a new one cause the Slater determinant being zero, we have:

$$\langle\Psi_0|\hat{O}_1|\Psi_0\rangle = \sum_{ab}\langle a|\hat{h}|b\rangle\langle\Psi_0|(\delta_{ab})|\Psi_0\rangle = \sum_{a}\langle a|\hat{h}|a\rangle$$

Double-particle operator

$$\hat{A} = \sum_{i<j}^{N} \hat{A}_{ij} \xrightarrow{\text{S.Q.}} \sum_{i<j}^{N} \hat{A}^{\dagger}_{ij} \quad \sum_{i<j}^{N} \hat{A}^{\dagger}_{ij} \phi_1^{\dagger} \cdots \phi_i^{\dagger} \cdots \phi_j^{\dagger} \cdots \phi_N^{\dagger} |0\rangle$$

$$= \sum_{i<j}^{N} \phi_1^{\dagger} \cdots \psi_i^{\dagger} \cdots \psi_j^{\dagger} \cdots \phi_N^{\dagger} |0\rangle$$

$$= \sum_{i<j}^{N} \sum_{k,l} C_{ij,kl} \phi_1^{\dagger} \cdots \phi_k^{\dagger} \cdots \phi_l^{\dagger} \cdots \phi_N^{\dagger} |0\rangle$$

From quantum mechanics of first quantization, we have known:

$$C_{ij,kl} = \iint \mathrm{d}^3 r \mathrm{d}^3 r' \phi_k(\boldsymbol{r}) \phi_l(\boldsymbol{r}') \frac{1}{|\boldsymbol{r} - \boldsymbol{r}'|} \phi_i(\boldsymbol{r}) \phi_j(\boldsymbol{r}') = \langle kl \,|\, ij \rangle$$

And we suppose $\sum_{i<j}^{N} \hat{A}^{\dagger}_{ij}$ has the expansion: $\sum_{i<j}^{N} \hat{A}^{\dagger}_{ij} = \sum_{i<j}^{N} \sum_{k,l} A_{ij,kl} \phi_k^{\dagger} \phi_l^{\dagger} \phi_i \phi_j$

Now let us try to find the relationship between $A_{ij,kl}$ and $C_{ij,kl}$.

$$\sum_{i<j}^{N}\sum_{k,l}(A_{ij,kl}\phi_k^\dagger\phi_l^\dagger\phi_i\phi_j)\phi_1^\dagger\cdots\phi_i^\dagger\cdots\phi_j^\dagger\cdots\phi_N^\dagger|0\rangle$$

$$=\sum_{i<j}^{N}\sum_{k,l}(A_{ij,kl}\phi_k^\dagger\phi_l^\dagger)(-1)^{i-1}(-1)^{j-1}\phi_1^\dagger\cdots\phi_{i-1}^\dagger\phi_{i+1}^\dagger\cdots\phi_{j-1}^\dagger\phi_{j+1}^\dagger\cdots\phi_N^\dagger|0\rangle$$

$$=\sum_{i<j}^{N}\sum_{k,l}(A_{ij,kl}\phi_k^\dagger)(-1)^{j-2}(-1)^{i-1}(-1)^{j-1}\phi_1^\dagger\cdots\phi_{i-1}^\dagger\phi_{i+1}^\dagger\cdots\phi_{j-1}^\dagger\phi_l^\dagger\phi_{j+1}^\dagger\cdots\phi_N^\dagger|0\rangle$$

$$=\sum_{i<j}^{N}\sum_{k,l}A_{ij,kl}(-1)^{(i-1)+(j-2)+(i-1)+(j-1)}\left[\phi_1^\dagger\cdots\phi_i^\dagger\cdots\phi_j^\dagger\cdots\phi_N^\dagger|0\rangle\right]$$

$$=\sum_{i<j}^{N}\sum_{k,l}(-A_{ij,kl})\left[\phi_1^\dagger\cdots\phi_i^\dagger\cdots\phi_j^\dagger\cdots\phi_N^\dagger|0\rangle\right]$$

$$A_{ij,kl}=-C_{ij,kl}$$

Example of the sign changing:

$$
\begin{aligned}
&\phi_3^\dagger \phi_5^\dagger \phi_3 \phi_5 \,|\, 1,2,3,4,5,6\rangle \\
&= (-1)^4 \phi_3^\dagger \phi_5^\dagger \phi_3 \,|\, 1,2,3,4,\times,6\rangle \\
&= (-1)^4 (-1)^2 \phi_3^\dagger \phi_5^\dagger \,|\, 1,2,\times,4,\times,6\rangle \\
&= (-1)^4 (-1)^2 (-1)^3 \phi_3^\dagger \,|\, 1,2,\times,4,5,6\rangle \\
&= (-1)^4 (-1)^2 (-1)^3 (-1)^2 \,|\, 1,2,3,4,5,6\rangle \\
&= -\,|\, 1,2,3,4,5,6\rangle
\end{aligned}
$$

Since when $i = j$, there would be two same annihilation operators:

$$\hat{A}^{\dagger}_{ii} = \sum_{k,l} A_{ii,kl} \phi^{\dagger}_{k} \phi^{\dagger}_{l} \phi_{i} \phi_{i} = \hat{0}$$

For fermion that is equal to zero, so we can remove the constraint $i < j$, and make the summation run over all the possibilities, and then divide by two.

$$\hat{A}^{\dagger}_{(\text{two-particle})} = \sum_{i<j}^{N} \hat{A}^{\dagger}_{ij} = -\frac{1}{2} \sum_{ijkl} C_{ij,kl} \phi^{\dagger}_{k} \phi^{\dagger}_{l} \phi_{i} \phi_{j} = -\frac{1}{2} \sum_{ijkl} \langle kl \,|\, ij \rangle \phi^{\dagger}_{k} \phi^{\dagger}_{l} \phi_{i} \phi_{j}$$

At last, we can use a trick to remove the minus sign using anti-commutation relation.

$$\hat{A}^{\dagger}_{(\text{two-particle})} = \sum_{i<j}^{N} \hat{A}^{\dagger}_{ij} = \frac{1}{2} \sum_{ijkl} \langle kl \,|\, ij \rangle \phi^{\dagger}_{k} \phi^{\dagger}_{l} \phi_{j} \phi_{i}$$

B-O Hamiltonian from Second quantization

Collect all the expressions

$$\hat{H} = \sum_i \hat{h}_i + \sum_{i<j} \frac{1}{r_{ij}}$$

$$= \sum_{\mu\nu} h_{\mu\nu} \hat{a}_\mu^\dagger \hat{a}_\nu + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle \mu\nu \,|\, \lambda\sigma \rangle \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\sigma \hat{a}_\lambda$$

$$\sum_i \hat{h}_i = \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j = \sum_{ij} h_{ij} (\delta_{ij} - \hat{a}_j \hat{a}_i^\dagger)$$

When considering ground state Slater determinant, since in it all possible i-positions are occupied, so that when create an electron at the i^{th} position, the determinant would be zero.

$$\hat{H} = \sum_i h_{ii} \hat{a}_i^\dagger \hat{a}_i + \frac{1}{2} \sum_{\mu\nu\lambda\sigma} \langle \mu\nu \,|\, \lambda\sigma \rangle \hat{a}_\mu^\dagger \hat{a}_\nu^\dagger \hat{a}_\sigma \hat{a}_\lambda$$

Verification of the two-body operator

$$|\Psi_0\rangle = |1\cdots a\cdots b\cdots N\rangle$$

$$\langle\Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{\mu\nu\lambda\sigma}\langle\mu\nu|\lambda\sigma\rangle\langle\Psi_0|\hat{a}_\mu^\dagger\hat{a}_\nu^\dagger\hat{a}_\sigma\hat{a}_\lambda|\Psi_0\rangle$$

Here we are considering the ground state,
so μ and ν must be within the set
$\{1,2,\cdots,a,\cdots,b,\cdots,N\}$:

$$\langle\Psi_0|\hat{O}_2|\Psi_0\rangle = \frac{1}{2}\sum_{abcd}\langle ab|cd\rangle\langle\Psi_0|\hat{a}_a^\dagger\hat{a}_b^\dagger\hat{a}_d\hat{a}_c|\Psi_0\rangle$$

$$\langle \Psi_0 | \hat{O}_2 | \Psi_0 \rangle = \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \hat{a}_a^\dagger (\delta_{bd} - \hat{a}_d \hat{a}_b^\dagger) \hat{a}_c | \Psi_0 \rangle$$

$$= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} \hat{a}_a^\dagger \hat{a}_c - \hat{a}_a^\dagger \hat{a}_d \hat{a}_b^\dagger \hat{a}_c | \Psi_0 \rangle$$

$$= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} (\delta_{ac} - \hat{a}_c \hat{a}_a^\dagger) - \hat{a}_a^\dagger \hat{a}_d (\delta_{bc} - \hat{a}_c \hat{a}_b^\dagger) | \Psi_0 \rangle$$

$$= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} \delta_{ac} - \delta_{bd} \hat{a}_c \hat{a}_a^\dagger - \hat{a}_a^\dagger \hat{a}_d \delta_{bc} + \hat{a}_a^\dagger \hat{a}_d \hat{a}_c \hat{a}_b^\dagger | \Psi_0 \rangle$$

$$= \frac{1}{2} \sum_{ab} \langle ab | cd \rangle \langle \Psi_0 | \delta_{bd} \delta_{ac} - \delta_{bc} (\delta_{ad} - \hat{a}_d \hat{a}_a^\dagger) | \Psi_0 \rangle$$

$$= \frac{1}{2} \sum_{ab} \left[\langle ab | ab \rangle - \langle ab | ba \rangle \right]$$

Back to main text

Suppose:

$\sigma_1(\omega) = \beta(\omega),\ \sigma_2(\omega) = \beta(\omega)$

$$\langle \Psi | \Psi \rangle = \langle 12 | 21 \rangle$$

$$= \frac{1}{2}(\langle 12| - \langle 21|)(|12\rangle - |21\rangle)$$

$$= \frac{1}{2}(1 - S - S + 1) = 1 - S$$

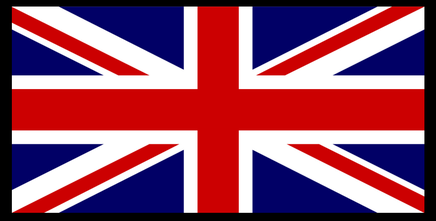
Fermi hole

$$\langle 12 | 21 \rangle = \iint \psi_1^*(\boldsymbol{r}_1)\beta_1^*(\omega_1)\psi_2^*(\boldsymbol{r}_2)\beta_2^*(\omega_2) \times$$

$$\psi_2(\boldsymbol{r}_1)\beta_2(\omega_1)\psi_1(\boldsymbol{r}_2)\beta_1(\omega_2)\mathrm{d}^3 r_1 \mathrm{d}^3 r_2$$

$$= \iint \psi_1^*(\boldsymbol{r}_1)\psi_2^*(\boldsymbol{r}_2)\psi_2(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2)\mathrm{d}^3 r_1 \mathrm{d}^3 r_2 = S$$

Hartree-Fock approximation



https://mathshistory.st-andrews.ac.uk/Biographies/Hartree/

https://physicstoday.scitation.org/do/10.1063/pt.6.6.20171222a/full/

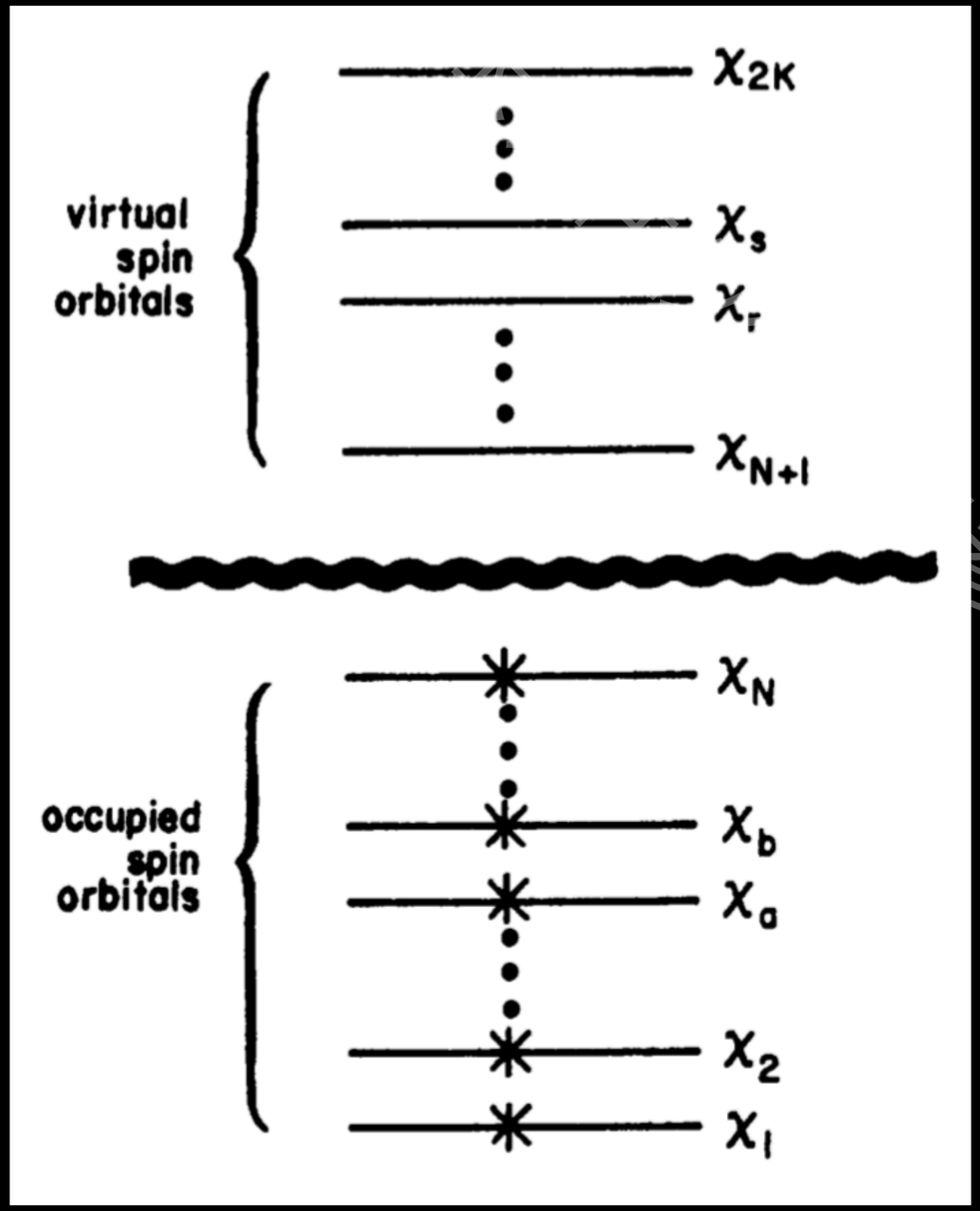
$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle$$

From variation principle, the best wave function of this functional form is the one which gives the lowest possible energy

$$E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle$$

Once one can ***optimize*** the wave function, one can obtain the best estimation from Hartree-Fock method.

$$\hat{f}(i)\chi(\boldsymbol{x}_i) = \varepsilon\chi(\boldsymbol{x}_i) \qquad \hat{f}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + v^{\mathrm{HF}}(i)$$



The Hartree-Fock ground state

$$|\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle$$

Minimal basis model

First, consider the atomic orbital:

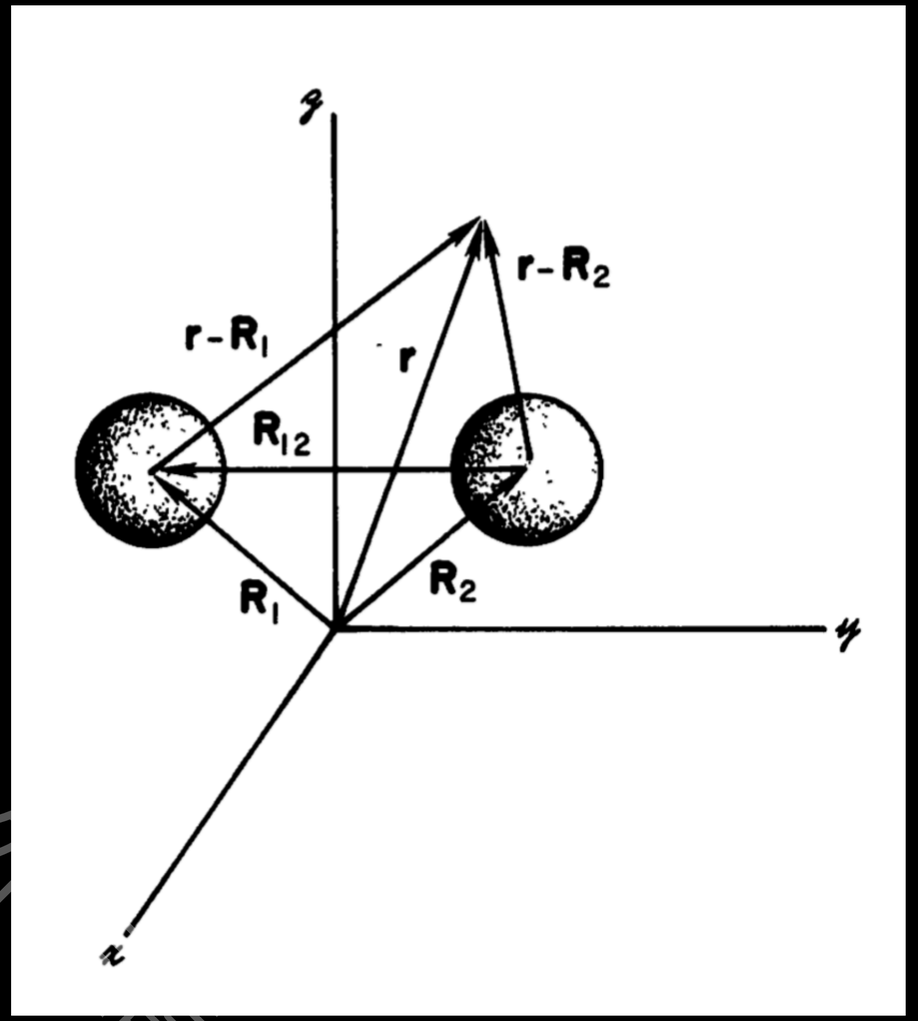
$$\phi_1 \equiv \phi_1(\boldsymbol{r} - \boldsymbol{R}_1) \qquad \phi_2 \equiv \phi_2(\boldsymbol{r} - \boldsymbol{R}_2)$$

Slater orbital: $$\phi(\boldsymbol{r} - \boldsymbol{R}) = \left(\frac{\zeta^3}{\pi}\right)^{1/2} e^{-\zeta|\boldsymbol{r}-\boldsymbol{R}|}$$

Gauss orbital:

$$\phi(\boldsymbol{r} - \boldsymbol{R}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} e^{-\alpha|\boldsymbol{r}-\boldsymbol{R}|^2}$$

$$\langle \phi_1 \,|\, \phi_2 \rangle = S$$

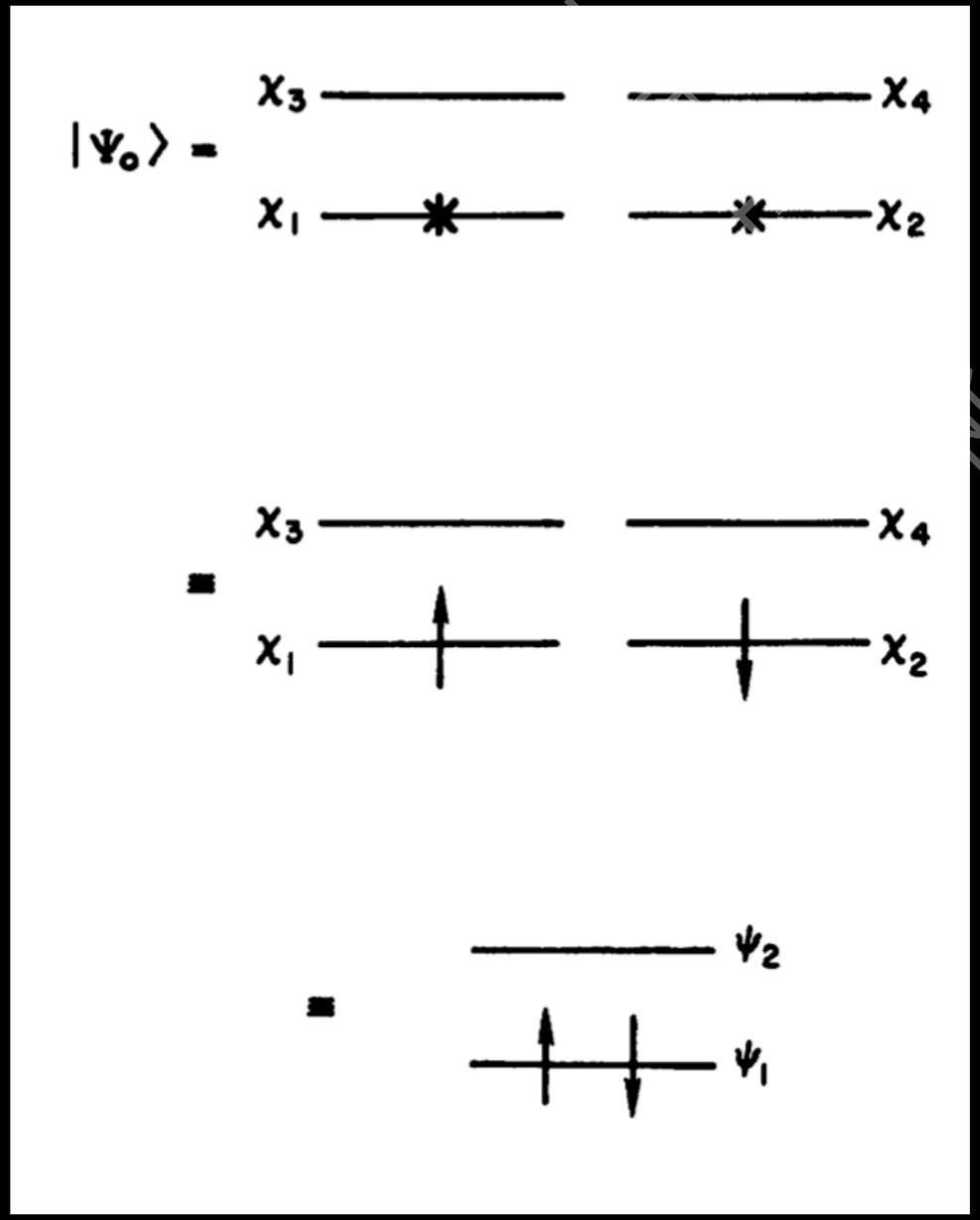


LCAO from the minimal basis

$$\psi_1 = [2(1+S)]^{-1/2}(\phi_1 + \phi_2)$$
$$\psi_2 = [2(1+S)]^{-1/2}(\phi_1 - \phi_2)$$

$$\chi_1 = \psi_1(\boldsymbol{r})\alpha(\omega)$$
$$\chi_2 = \psi_1(\boldsymbol{r})\beta(\omega)$$
$$\chi_3 = \psi_2(\boldsymbol{r})\alpha(\omega)$$
$$\chi_4 = \psi_2(\boldsymbol{r})\beta(\omega)$$

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle$$



$$|\Psi_0\rangle = |\chi_1\chi_2\rangle$$

$$\chi_1 \equiv \psi_1, \quad \chi_2 \equiv \bar{\psi}_1$$
$$\chi_3 \equiv \psi_2, \quad \chi_4 \equiv \bar{\psi}_2$$

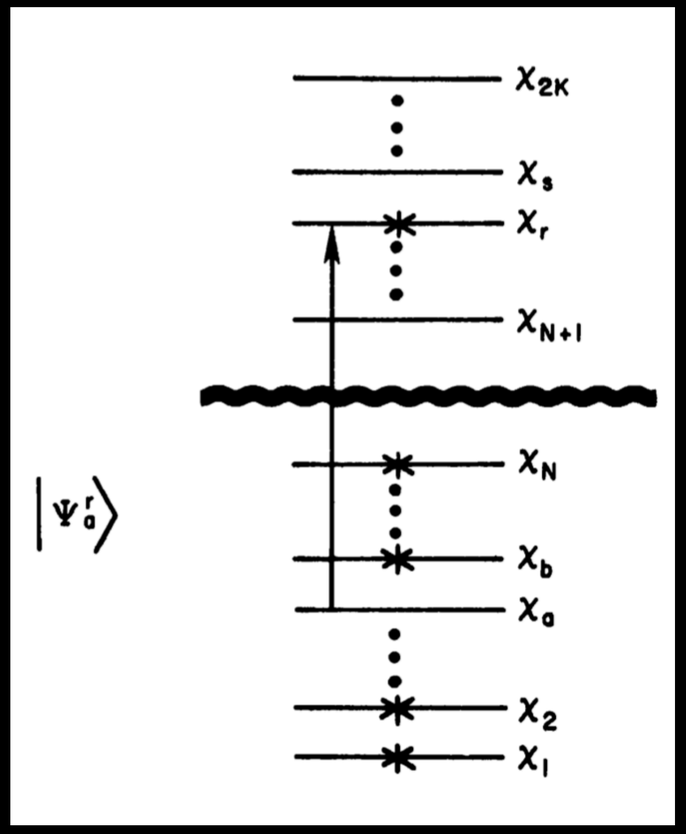
$$|\Psi_0\rangle = |\psi_1\bar{\psi}_1\rangle$$

Excited Determinants

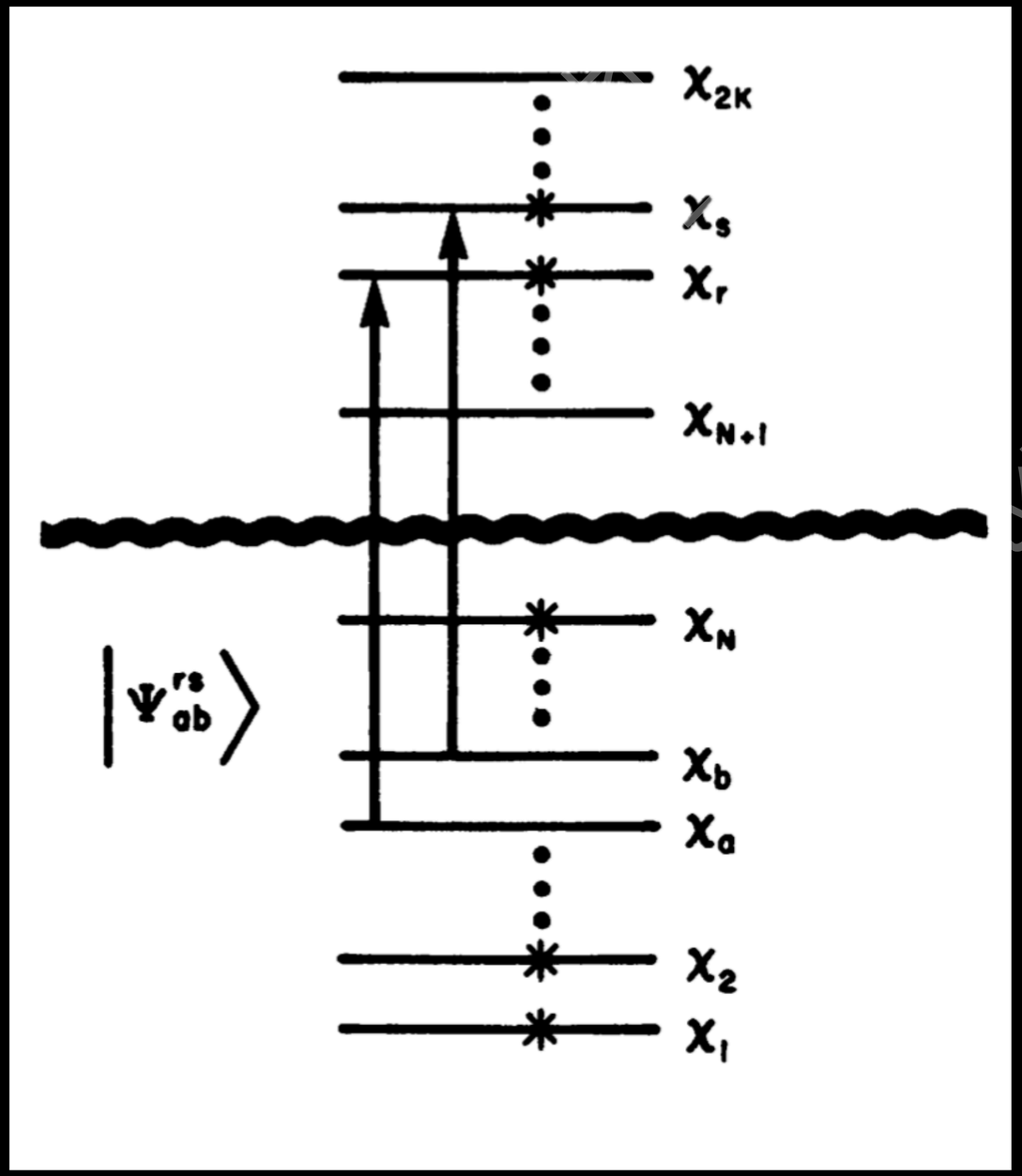
$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_a\chi_b\cdots\chi_N\rangle$$

With $2K$ orbitals and N electrons, there are multiple different Slater determinants:

$$\binom{2K}{N} = \frac{(2K)!}{N!(2K-N)!}$$



After H-F calculation, the energy of each χ_i is fixed. So the choices different from the ground state Slater determinant can be explained as excitation.



$$|\Psi_a^r\rangle = |\chi_1\chi_2\cdots\chi_r\chi_b\cdots\chi_N\rangle$$

$$|\Psi_{ab}^{rs}\rangle = |\chi_1\chi_2\cdots\chi_r\chi_s\cdots\chi_N\rangle$$

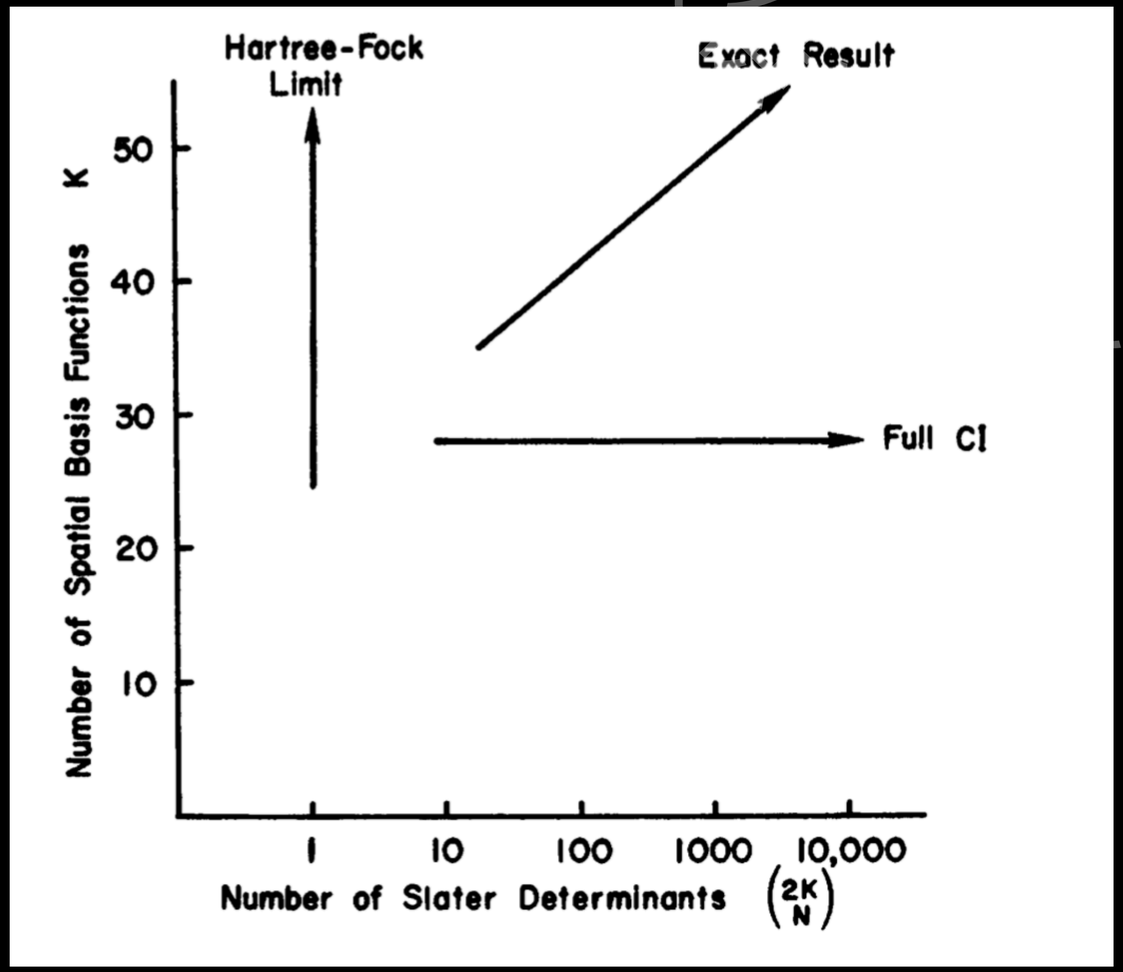
$$|\Phi\rangle = c_0|\Psi_0\rangle + \sum_{ra} c_a^r|\Psi_a^r\rangle + \sum_{a<b,r<s} c_{ab}^{rs}|\Psi_{ab}^{rs}\rangle + \cdots$$

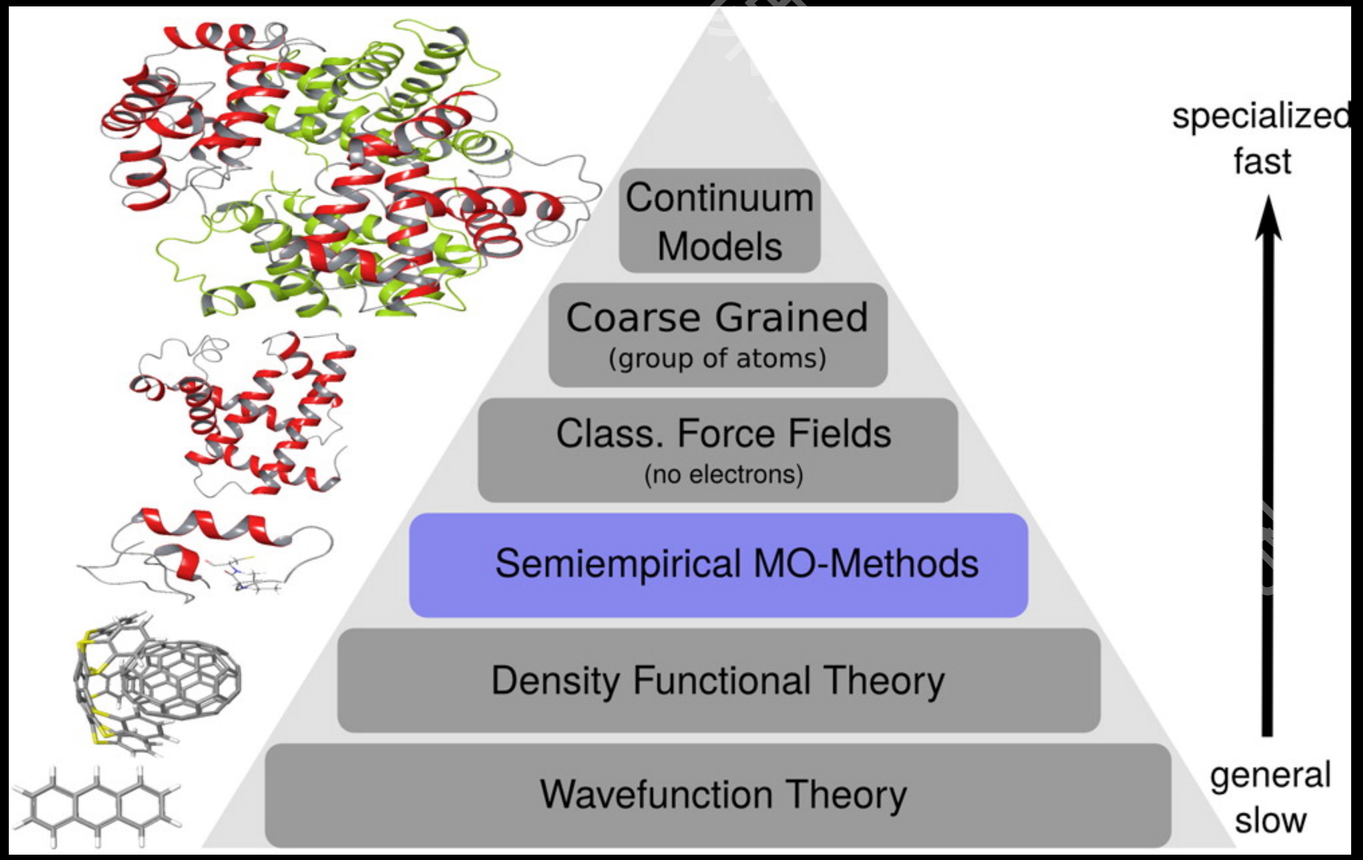
Consider the possible choices of S-D, this is called ***configuration interaction*** (CI).
Taking into the full account of choices is named full-CI.

Correlation energy

$$E^{\text{corr}} \equiv E^{\text{real}} - E_0$$

Energy from Hartree-Fock limit





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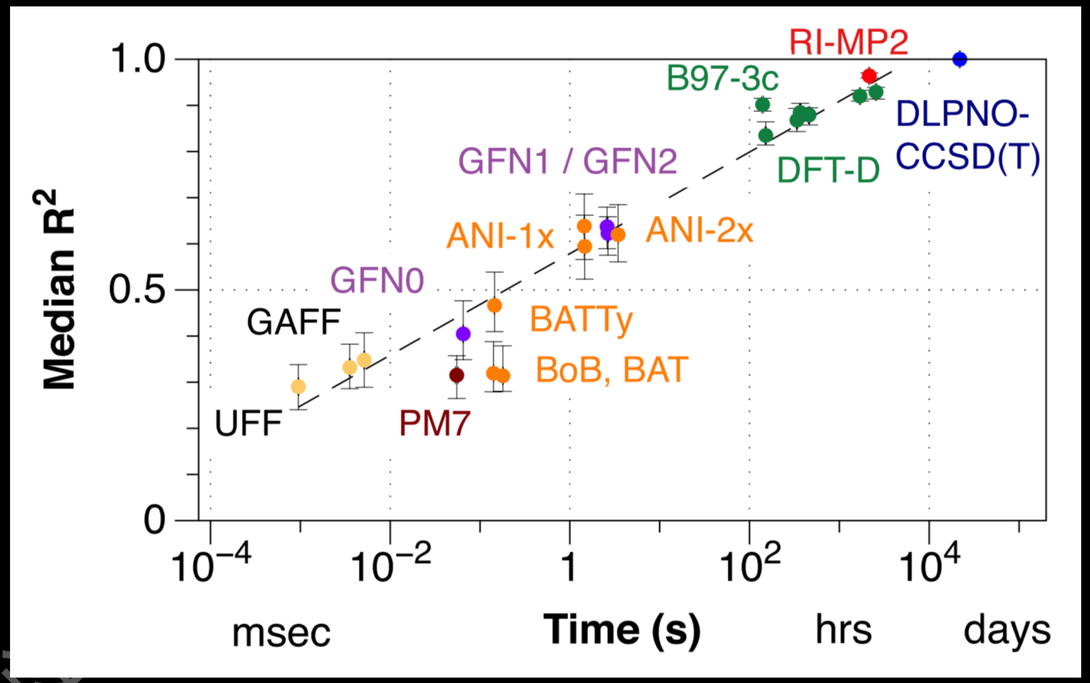

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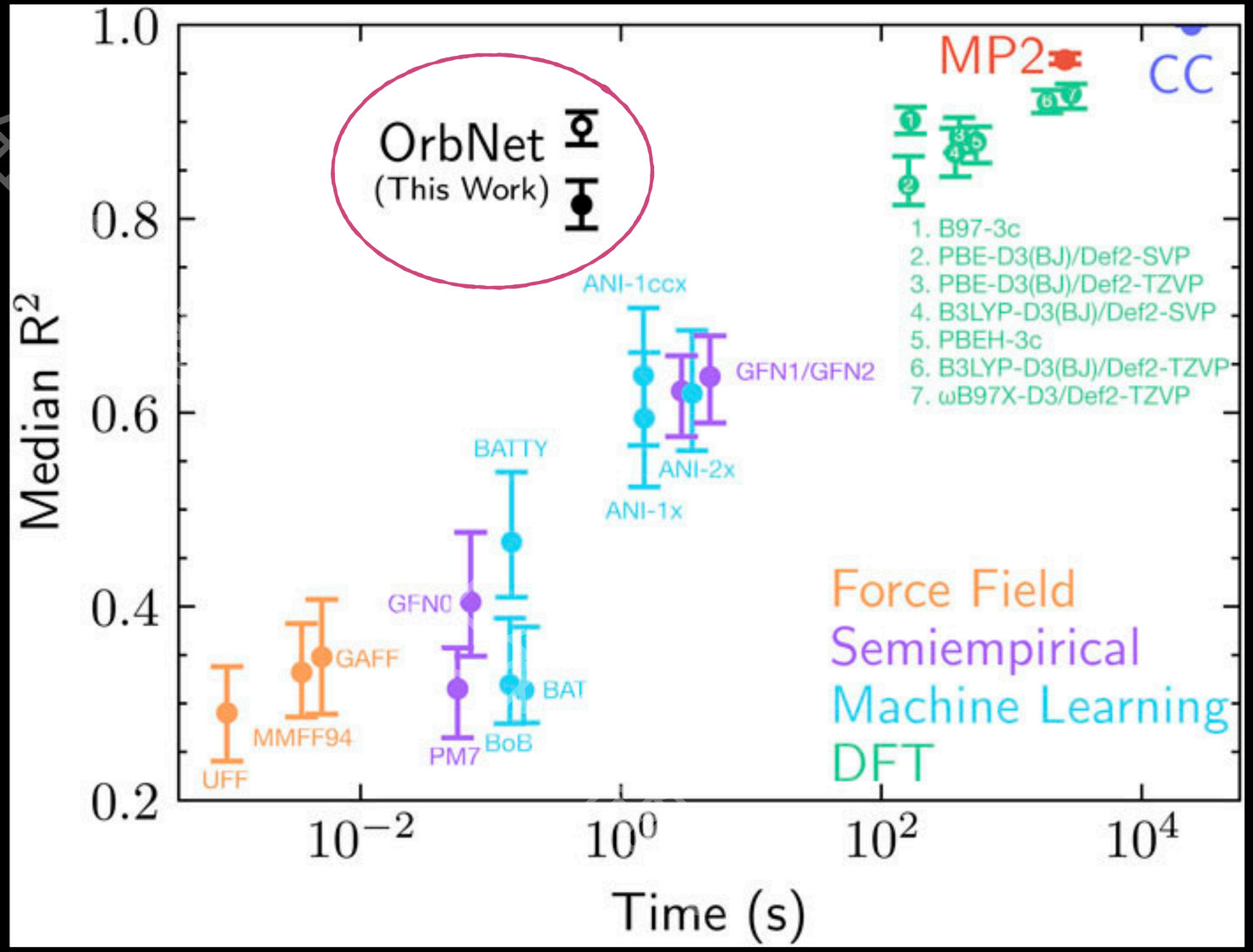
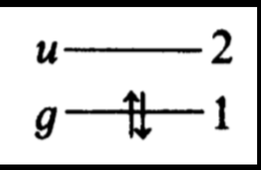


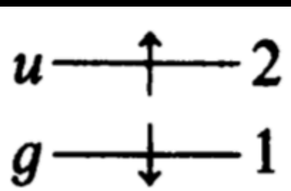
Examples of S-Ds in minimal basis of H_2

$$\binom{2*2}{2} = \frac{(4)!}{2!(2*2-2)!} = 6$$

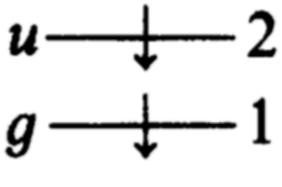
$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle = |1\bar{1}\rangle$



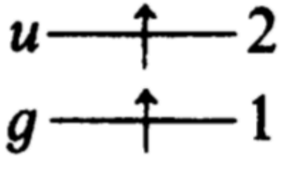
$|\Psi_1^2\rangle = |2\bar{1}\rangle$



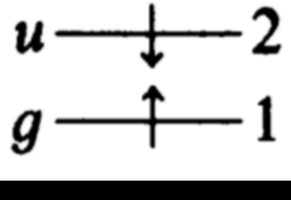
$|\Psi_1^{\bar{2}}\rangle = |\bar{2}1\rangle$



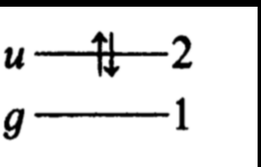
$|\Psi_{\bar{1}}^2\rangle = |12\rangle$



$|\Psi_{\bar{1}}^{\bar{2}}\rangle = |1\bar{2}\rangle$



$|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = |2\bar{2}\rangle = |\chi_3\chi_4\rangle = |\Psi_{12}^{34}\rangle$



$$|\Phi_0\rangle = c_0|\Psi_0\rangle + c_{1\bar{1}}^{2\bar{2}}|\Psi_{1\bar{1}}^{2\bar{2}}\rangle = c_0|\Psi_0\rangle + c_{12}^{34}|\Psi_{12}^{34}\rangle$$

Operators and Matrix Elements

From the minimal basis of H_2

$$\hat{H} = \left(-\frac{1}{2}\nabla_1^2 - \frac{Z_A}{r_{1A}} - \frac{Z_B}{r_{1B}}\right) + \left(-\frac{1}{2}\nabla_2^2 - \frac{Z_A}{r_{2A}} - \frac{Z_B}{r_{1B}}\right) + \frac{1}{r_{12}}$$

$$= \boxed{\hat{h}(1) + \hat{h}(2)} + \frac{1}{r_{12}}$$

Core-Hamiltonian

One-body operator

Two-body operator

$$\hat{\mathcal{O}}_1 = \hat{h}(1) + \hat{h}(2)$$

$$\hat{\mathcal{O}}_2 = \frac{1}{r_{12}}$$

$$\langle \Psi_0 | \hat{h}(1) | \Psi_0 \rangle = \int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \left\{ 2^{-1/2} \left[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2) - \chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2) \right] \right\}^* \times$$

$$\hat{h}(\boldsymbol{r}_1) \left\{ 2^{-1/2} \left[\chi_1(\boldsymbol{x}_1)\chi_2(\boldsymbol{x}_2) - \chi_2(\boldsymbol{x}_1)\chi_1(\boldsymbol{x}_2) \right] \right\}$$

Simplified denotation:

$\chi_\alpha(\boldsymbol{x}_1)\chi_\beta(\boldsymbol{x}_2) \equiv \chi_\alpha \chi_\beta$

$$= \frac{1}{2} \int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \left\{ \chi_1^* \chi_2^* \hat{h}(\boldsymbol{r}_1) \chi_1 \chi_2 + \chi_2^* \chi_1^* \hat{h}(\boldsymbol{r}_1) \chi_2 \chi_1 \right.$$

$$\left. - \chi_1^* \chi_2^* \hat{h}(\boldsymbol{r}_1) \chi_2 \chi_1 - \chi_2^* \chi_1^* \hat{h}(\boldsymbol{r}_1) \chi_1 \chi_2 \right\}$$

$$\int \mathrm{d}\boldsymbol{x}_2 \chi_2^*(\boldsymbol{x}_2)\chi_1(\boldsymbol{x}_2) = 0$$

$$\int \mathrm{d}\boldsymbol{x}_2 \chi_1^*(\boldsymbol{x}_2)\chi_2(\boldsymbol{x}_2) = 0$$

$$\langle \Psi_0 | \hat{h}(1) | \Psi_0 \rangle = \frac{1}{2} \langle 1 | \hat{h}(1) | 1 \rangle + \frac{1}{2} \langle 2 | \hat{h}(1) | 2 \rangle$$

One can prove: $\langle \Psi_0 | \hat{h}(2) | \Psi_0 \rangle = \langle \Psi_0 | \hat{h}(1) | \Psi_0 \rangle$

$$\langle \Psi_0 | \hat{\mathcal{O}}_1 | \Psi_0 \rangle = \langle 1 | \hat{h}(1) | 1 \rangle + \langle 2 | \hat{h}(1) | 2 \rangle$$
$$= \langle 1 | \hat{h} | 1 \rangle + \langle 2 | \hat{h} | 2 \rangle$$

One can also prove:

$$\langle \Psi_{12}^{34} | \hat{\mathcal{O}}_1 | \Psi_{12}^{34} \rangle = \langle 3 | \hat{h} | 3 \rangle + \langle 4 | \hat{h} | 4 \rangle$$

$$\langle \Psi_{12}^{34} | \hat{\mathcal{O}}_1 | \Psi_0 \rangle = 0$$

$$\langle \Psi_0 | \hat{\mathcal{O}}_2 | \Psi_0 \rangle = \frac{1}{2} \int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \left\{ [\chi_1\chi_2 - \chi_2\chi_1]^* \frac{1}{r_{12}} [\chi_1\chi_2 - \chi_2\chi_1] \right\}$$

$$= \frac{1}{2} \int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \left\{ \chi_1^*\chi_2^* \frac{1}{r_{12}} \chi_1\chi_2 + \chi_2^*\chi_1^* \frac{1}{r_{12}} \chi_2\chi_1 \right.$$

$$\left. - \chi_1^*\chi_2^* \frac{1}{r_{12}} \chi_2\chi_1 - \chi_2^*\chi_1^* \frac{1}{r_{12}} \chi_1\chi_2 \right\}$$

Since $r_{12} = r_{21}$

$$= \boxed{\int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \chi_1^*\chi_2^* \frac{1}{r_{12}} \chi_1\chi_2 - \int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \chi_1^*\chi_2^* \frac{1}{r_{12}} \chi_2\chi_1}$$

Two-electron integral

Notation of two-electron integrals

$$\langle ij \,|\, kl \rangle = \langle \chi_i \chi_j \,|\, \chi_k \chi_l \rangle$$

$$= \int \mathrm{d}\boldsymbol{x}_1 \mathrm{d}\boldsymbol{x}_2 \; \chi_i^*(\boldsymbol{x}_1) \chi_j^*(\boldsymbol{x}_2) \frac{1}{r_{12}} \chi_k(\boldsymbol{x}_1) \chi_l(\boldsymbol{x}_2)$$

$$\langle \Psi_0 \,|\, \hat{\mathcal{O}}_2 \,|\, \Psi_0 \rangle = \langle 12 \,|\, 12 \rangle - \langle 12 \,|\, 21 \rangle$$

Some properties

$$\langle ij|kl\rangle = \langle ji|lk\rangle \qquad \langle ij|kl\rangle = \langle kl|ij\rangle^*$$

Anti-symmetrized two-electron integral

$$\langle ij||kl\rangle = \langle ij|kl\rangle - \langle ij|lk\rangle$$

$$\langle ij||kk\rangle = \langle ij|kk\rangle - \langle ij|kk\rangle = 0$$

Transition from spin orbital to spatial orbital

$$|\Psi_0\rangle = |\chi_1\chi_2\rangle = |\psi_1\bar{\psi}_1\rangle$$

$$E_0 = \langle\chi_1|h|\chi_1\rangle + \langle\chi_2|h|\chi_2\rangle + \langle\chi_1\chi_2|\chi_1\chi_2\rangle - \langle\chi_1\chi_2|\chi_2\chi_1\rangle$$

$$E_0 = \langle 1|\hat{h}|1\rangle + \langle\bar{1}|\hat{h}|\bar{1}\rangle + \langle 1\bar{1}|1\bar{1}\rangle - \langle 1\bar{1}|\bar{1}1\rangle$$

$$E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle = \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_{ab}\langle ab||ab\rangle$$

Since $\langle aa||aa\rangle = 0$, and $\langle ab||ab\rangle = \langle ba||ba\rangle$, so: $\sum_{a<b}\langle ab||ab\rangle = \frac{1}{2}\sum_{ab}\langle ab||ab\rangle$

$$\langle 1\bar{1} \,|\, 1\bar{1}\rangle = \int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\omega_1 \mathrm{d}\boldsymbol{r}_2 \mathrm{d}\omega_2 \psi_1^*(\boldsymbol{r}_1)\alpha^*(\omega_1)\psi_1^*(\boldsymbol{r}_1)\beta^*(\omega_1)$$

$$\frac{1}{r_{12}}\psi_1(\boldsymbol{r}_1)\alpha(\omega_1)\psi_1(\boldsymbol{r}_2)\beta(\omega_2)$$

$$= \int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \psi_1^*(\boldsymbol{r}_1)\psi_1^*(\boldsymbol{r}_1)\frac{1}{r_{12}}\psi_1(\boldsymbol{r}_1)\psi_1(\boldsymbol{r}_2) = (11 \,|\, 11)$$

$$\langle 1\bar{1} \,|\, \bar{1}1\rangle = \int \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\omega_1 \mathrm{d}\boldsymbol{r}_2 \mathrm{d}\omega_2 \psi_1^*(\boldsymbol{r}_1)\alpha^*(\omega_1)\psi_1^*(\boldsymbol{r}_1)\beta^*(\omega_1)$$

$$\frac{1}{r_{12}}\psi_1(\boldsymbol{r}_1)\beta(\omega_1)\psi_1(\boldsymbol{r}_2)\alpha(\omega_2) = 0$$

$$\langle ik|jl\rangle = (ij|kl)$$

$$E_0 = 2(\psi_1|\hat{h}|\psi_1) + (\psi_1\psi_1|\psi_1\psi_1)$$

$$= 2(1|\hat{h}|1) + (11|11)$$

$$E_0 = 2\sum_{a}^{N/2}(a|h|a) + \sum_{a}^{N/2}\sum_{b}^{N/2}\left[2(aa|bb) - (ab|ba)\right]$$

Coulomb integral and Exchange integral

$$J_{ij} = (ii|jj) = \langle ij|ij\rangle$$

$$K_{ij} = (ij|ji) = \langle ij|ji\rangle$$

Hartree-Fock equation

Collection of what we have

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle$$

$$\chi_i(\vec{r}) = \sigma_i(\omega)\sum_{\alpha=1}^{N} c_{i\alpha}\phi_\alpha(\vec{r})$$

$$\langle a|h|a\rangle = \int \psi_a^*(\vec{r})\left(-\frac{1}{2}\nabla^2 - \sum_{A=1}^{M}\frac{Z_A}{r_{a,A}}\right)\psi_a(\vec{r})\mathrm{d}^3r\langle\sigma_a|\sigma_a\rangle$$

$$\langle ab||ab\rangle = \iint \psi_a^*(\vec{r}_1)\psi_b^*\left[(\vec{r}_2)\frac{1}{r_{12}}\psi_a(\vec{r}_1)\psi_b(\vec{r}_2)\langle\sigma_a|\sigma_a\rangle\langle\sigma_b|\sigma_b\rangle - \psi_b(\vec{r}_1)\psi_a(\vec{r}_2)\langle\sigma_a|\sigma_b\rangle\langle\sigma_b|\sigma_a\rangle\right]\mathrm{d}^3r_1\mathrm{d}^3r_2$$

$$\chi_i(\vec{r}) = \sigma_i(\omega) \sum_{\alpha=1}^{N} c_{i\alpha}\phi_\alpha(\vec{r})$$

Example (fixed coefficients):

$$\psi_1 = [2(1+S)]^{-1/2}(\phi_1 + \phi_2) \qquad S = \langle \phi_1 | \phi_2 \rangle \qquad \chi_1 = \psi_1(\boldsymbol{r})\alpha(\omega)$$

$$\psi_2 = [2(1+S)]^{-1/2}(\phi_1 - \phi_2) \qquad \chi_2 = \psi_1(\boldsymbol{r})\beta(\omega)$$

$$\chi_3 = \psi_2(\boldsymbol{r})\alpha(\omega)$$

$$\chi_4 = \psi_2(\boldsymbol{r})\beta(\omega)$$

$$\phi_1(\vec{r}) = \frac{1}{\sqrt{\pi}} e^{-|\vec{r}-\vec{R}_1|}$$

$$\phi_2(\vec{r}) = \frac{1}{\sqrt{\pi}} e^{-|\vec{r}-\vec{R}_2|}$$

Matrix elements

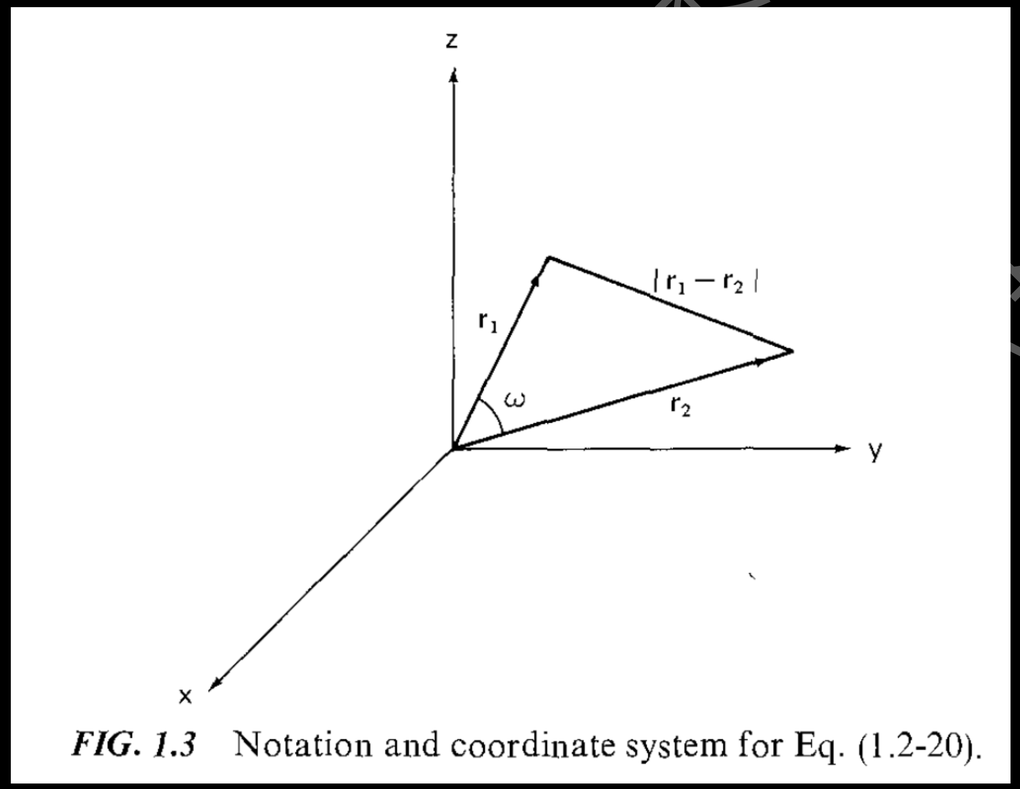


FIG. 1.3 Notation and coordinate system for Eq. (1.2-20).

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{l=0}^{\infty} \frac{r_<^l}{r_>^{l+1}} P_l(\cos\omega)$$

In which $r_<$ stands for the smaller of the two distances $|\vec{r}_1|$ and $|\vec{r}_2|$, $r_>$ is the greater of the two distances, and $P_l(\cos\omega)$ is a Legendre polynomial.

Since $\vec{r}_1 = (r_1, \theta_1, \varphi_1)$ and $\vec{r}_2 = (r_2, \theta_2, \varphi_2)$, then the angle ω is the angle between the two directions. The addition theorem:

$$P_l(\cos\omega) = \frac{4\pi}{2l+1} \sum_{m=-l}^{l} Y_{lm}^*(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

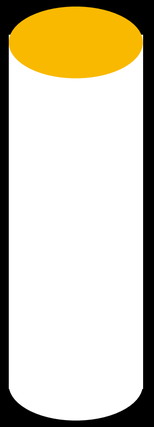
$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\theta_1, \varphi_1) Y_{lm}(\theta_2, \varphi_2)$$

Distraction: Lagrange multiplier

A cylinder, with its radius r and height h, given its surface known as 6π, what's its largest volume?

$$V = \pi r^2 h \qquad S = 2\pi rh + 2\pi r^2 = 6\pi$$

$$\mathscr{L} = V - \lambda(S - 6\pi) = \pi r^2 h - \lambda(2\pi rh + 2\pi r^2 - 6\pi)$$



$$\frac{\partial \mathscr{L}}{\partial r} = 2\pi rh - \lambda(2\pi h + 4\pi r) = 0 \qquad rh - \lambda h - 2\lambda r = 0$$

$$\frac{\partial \mathscr{L}}{\partial h} = \pi r^2 - \lambda(2\pi r) = 0 \qquad r = 2\lambda \qquad h = 4\lambda \qquad \lambda = \frac{1}{2} \qquad \begin{cases} h = 2 \\ r = 1 \end{cases}$$

$$|\Psi_0\rangle = |\chi_1\chi_2\cdots\chi_N\rangle \qquad E_0 = \langle\Psi_0|\hat{H}|\Psi_0\rangle = \sum_a \langle a|h|a\rangle + \frac{1}{2}\sum_{ab}\langle ab||ab\rangle$$

$$\langle a|b\rangle = \delta_{ab}$$

$$\mathscr{L} = E_0[\{\chi_a\}] - \sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ba}(\langle a|b\rangle - \delta_{ab})$$

$$\delta\mathscr{L} = \delta E_0[\{\chi_a\}] - \sum_{a=1}^{N}\sum_{b=1}^{N}\varepsilon_{ba}\delta\langle a|b\rangle = 0$$

$$\delta\langle a|b\rangle = \langle \delta a|b\rangle + \langle a|\delta b\rangle = \langle \delta a|b\rangle + c.c.$$

$$\delta E_0 = \sum_{a=1}^{N}\left[\langle \delta a|h|a\rangle + \langle a|h|\delta a\rangle\right] \qquad \langle \delta a|h|a\rangle = \langle a|h|\delta a\rangle^*$$

$$+\frac{1}{2}\sum_{a,b}\left[\langle (\delta a)b|ab\rangle + \langle a(\delta b)|ab\rangle + \langle ab|(\delta a)b\rangle + \langle ab|a(\delta b)\rangle\right]$$

$$-\frac{1}{2}\sum_{a,b}\left[\langle (\delta a)b|ba\rangle + \langle a(\delta b)|ba\rangle + \langle ab|(\delta b)a\rangle + \langle ab|b(\delta a)\rangle\right]$$

$$\langle ij|kl\rangle = \langle ji|lk\rangle$$

$$\Rightarrow \langle a(\delta b)|ab\rangle = \langle (\delta b)a|ba\rangle$$

$$\sum_{ab}\langle (\delta b)a|ba\rangle = \sum_{ba}\langle (\delta a)b|ab\rangle$$

$$= \sum_{ab}\langle (\delta a)b|ab\rangle$$

$$\delta E_0 = \sum_{a=1}^{N} \langle \delta a | h | a \rangle + \sum_{a,b} \langle (\delta a) b | ab \rangle - \sum_{a,b} \langle (\delta a) b | ba \rangle$$
$$+ c.c.$$

$$\delta \mathscr{L} = \sum_{a=1}^{N} \langle \delta a | h | a \rangle + \sum_{a,b} \left[\langle (\delta a) b | ab \rangle - \langle (\delta a) b | ba \rangle \right]$$
$$- \sum_{ab} \varepsilon_{ab} \langle \delta a | b \rangle + c.c. = 0$$

$$= \sum_{a=1}^{N} \left\{ \langle \delta a | h | a \rangle + \sum_{b=1}^{N} \left[\langle (\delta a) b | ab \rangle - \langle (\delta a) b | ba \rangle \right] \right.$$
$$\left. - \sum_{b=1}^{N} \varepsilon_{ab} \langle \delta a | b \rangle \right\} + c.c. = 0$$

$$\delta\mathscr{L} = \sum_{a=1}^{N}\int \mathrm{d}\boldsymbol{x}_1(\delta\chi_a^*)\left\{\hat{h}\chi_a + \sum_{b=1}^{N}\left[\hat{\mathscr{J}}_b - \hat{\mathscr{K}}_b\right]\chi_a - \sum_{b=1}^{N}\varepsilon_{ab}\chi_b\right\} + c.c. = 0$$

$$\hat{h}\chi_a + \sum_{b=1}^{N}\left[\hat{\mathscr{J}}_b - \hat{\mathscr{K}}_b\right]\chi_a = \sum_{b=1}^{N}\varepsilon_{ab}\chi_b$$

$$\hat{\mathscr{J}}_b\chi_a = \hat{\mathscr{J}}_b(1)\chi_a(1) = \left[\int \mathrm{d}\boldsymbol{x}_2\chi_b^*(2)r_{12}^{-1}\chi_b(2)\right]\chi_a(1)$$

$$\hat{\mathscr{K}}_b\chi_a = \hat{\mathscr{K}}_b(1)\chi_a(1) = \left[\int \mathrm{d}\boldsymbol{x}_2\chi_b^*(2)r_{12}^{-1}\chi_a(2)\right]\chi_b(1)$$

$$\hat{h}\chi_a + \sum_{b=1}^{N}\left[\hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b\right]\chi_a = \sum_{b=1}^{N}\varepsilon_{ab}\chi_b$$

Fock operator:

$$\hat{\mathcal{F}} = \hat{h} + \sum_{b=1}^{N}\left[\hat{\mathcal{J}}_b - \hat{\mathcal{K}}_b\right]$$

Hartree-Fock equation:

$$\hat{\mathcal{F}}\chi_a = \sum_{b=1}^{N}\varepsilon_{ab}\chi_b$$

Canonical H-F equation

$$\chi'_a = \sum_b \chi_b U_{ba} \qquad |\Psi'_0\rangle = \det(\mathbf{U})\,|\Psi_0\rangle$$

$$\mathbf{U}^\dagger\mathbf{U} = \mathbf{1} \qquad \det\left[\mathbf{U}^\dagger\mathbf{U}\right] = |\det(\mathbf{U})|^2 = 1 \qquad \det(\mathbf{U}) = e^{i\phi} \quad (\pm 1)$$

$$\sum_a \hat{\mathcal{J}}'_a(1) = \sum_a \int \mathrm{d}\boldsymbol{x}_2 \chi'^*_b(2) r_{12}^{-1} \chi'_b(2) \qquad \sum_a U^*_{ba} U_{ca} = (\mathbf{U}\mathbf{U}^\dagger)_{cb} = \delta_{cb}$$

$$= \sum_{bc} \left[\sum_a U^*_{ba} U_{ca} \right] \int \mathrm{d}\boldsymbol{x}_2 \chi^*_b(2) r_{12}^{-1} \chi_b(2) = \sum_a \hat{\mathcal{J}}_a(1)$$

$$\hat{\mathscr{F}}' = \hat{\mathscr{F}}$$

$$\varepsilon' = \mathbf{U}^{\dagger}\varepsilon\mathbf{U}$$

$$\hat{\mathscr{F}}\,|\chi'_a\rangle = \varepsilon'_a\,|\chi'_a\rangle$$

End