

The hydrogen molecule and the Hartree-Fock method

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RPI

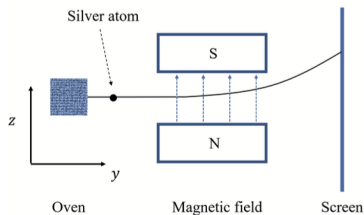
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Outline

- ▶ Review
 - ▶ Stern-Gerlach
 - ▶ Pauli Matricies
 - ▶ Spin 1/2 Particles
- ▶ H_2^+
- ▶ Identical Particles
- ▶ H_2 (Two Spin 1/2 Particles)
- ▶ Hartree Fock

Stern-Gerlach

- ▶ Hot Silver atoms in an oven
- ▶ Heating causes the silver to lose a valence electron and have a magnetic moment $\mu \in \mathbb{R}$
- ▶ Homogeneous magnetic field in the z-direction



- ▶ What pattern do we expect to see on the screen?

Stern-Gerlach Results



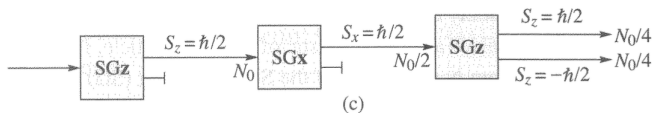
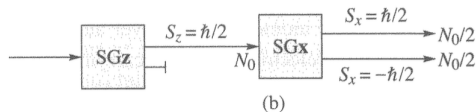
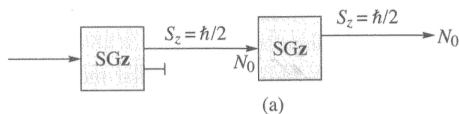
(a) Classical prediction



(b) Experiment

Stern-Gerlach Results Part 2

- ▶ Create a filter using this magnet, block one channel (either up or down).
- ▶ Feed in $|+z\rangle$ and get out $|+z\rangle$ and $| -z\rangle$ states!



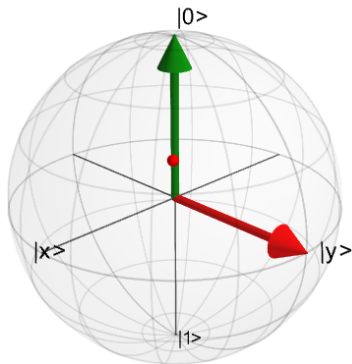
Spin 1/2 States

- ▶ Quantum Mechanics-the branch of mechanics that deals with the mathematical description of the motion and interaction of subatomic particles, incorporating the concepts of **quantization of energy**, wave-particle duality, the uncertainty principle, and the correspondence principle.-
- ▶ The spin 1/2 particle is a 2D vector on a hilbert space \mathcal{H} isomorphic to \mathbb{C}^2

$$\begin{aligned} |\psi\rangle &= c_1 |+\mathbf{z}\rangle + c_2 |-\mathbf{z}\rangle \\ |\psi\rangle &= c_1 |\uparrow\rangle + c_2 |\downarrow\rangle \end{aligned}$$

- ▶ Dot product: $\langle +\mathbf{z} | +\mathbf{z} \rangle = \langle -\mathbf{z} | -\mathbf{z} \rangle = 1$, $\langle +\mathbf{z} | -\mathbf{z} \rangle = 0$
- ▶ $|\psi\rangle = \sum_{i=1}^n c_i |\varphi_i\rangle$, $c_i \in \mathbb{C}$
- ▶ $|c_i|^2$ is the probability of being in the state $|\varphi_i\rangle$

Bloch Sphere



Spin Operators

- ▶ $\hat{A}|\varphi\rangle = a|\varphi\rangle$, where a is an observable/measurable quantity
- ▶ Expectation Value of $\langle\hat{A}\rangle = \langle\psi|\hat{A}|\psi\rangle = \sum_{i=1}^n a_i|c_i|^2$
- ▶ Pauli Matrices(Spin Operators):
 - ▶ Common state vectors $|\pm z\rangle, |\pm x\rangle, |\pm y\rangle$ have corresponding observable values $\pm\frac{\hbar}{2}$ or ± 1 depicted below
 - ▶ In the z-basis, these can be represented as:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$$\sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}$$

$$\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Rotations

- ▶ Why are the spin operators called the generators of rotations?

- ▶ $R(d\phi\hat{k}) = 1 + \frac{i}{\hbar}S_z d\phi$

- ▶ $d\phi \rightarrow \lim_{N \rightarrow \infty}$

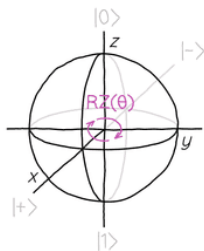
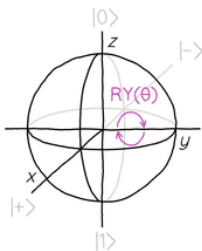
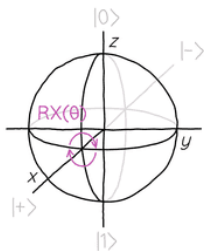
- ▶ Illegal notation $R(\phi\hat{k}) = \lim_{N \rightarrow \infty} [1 - \frac{i}{\hbar}S_z(\frac{\phi}{N})]^N = e^{-i\hat{S}_z\phi/\hbar}$

- ▶ Expand the exponential:

- $\hat{R}(\phi\hat{k})|+z\rangle = [1 - \frac{i\phi S_z}{\hbar} + \frac{1}{2!}(-\frac{i\phi S_z}{\hbar})^2 + \dots]|+z\rangle$

Geometrical Approach to a New Basis

- ▶ $\hat{R}(\frac{\pi}{2}\hat{j}) | +z \rangle = | -x \rangle$
- ▶ $| +x \rangle = \frac{1}{\sqrt{2}} (| +z \rangle + | -z \rangle)$
- ▶ $| +y \rangle = \frac{1}{\sqrt{2}} (| +z \rangle + i | -z \rangle)$



The Hydrogen Atom Revisited

- ▶ $E_n = -\frac{1}{2(k+l)^2}$ where $n = k + l$
- ▶ Let $0 < l < n$ and $-l \leq m \leq l$ where $n = 1, 2, 3, \dots$
- ▶ We find that the lowest energy eigenvalue corresponds to $n = 1, l = 0, m = 0$ with energy $E_0 = -\frac{1}{2}$
- ▶ Referring to last lecture, we know that $V(r)|_{l=0} = \lim_{r \rightarrow \infty} \frac{l(l+1)}{2r^2} |_{l=0} - \frac{1}{r} = 1 - \frac{1}{r}$
- ▶ The eigenvalue problem now becomes:
$$-\frac{1}{2} \frac{\partial^2 u}{\partial r^2} + \left(1 - \frac{1}{r}\right)u = Eu$$
- ▶ Using $u(r) = re^{-r}$:

$$\frac{1}{2}e^{-r} - e^{-r}r + re^{-r} - \frac{1}{r}re^{-r} = -\frac{1}{2}re^{-r} \quad (1)$$

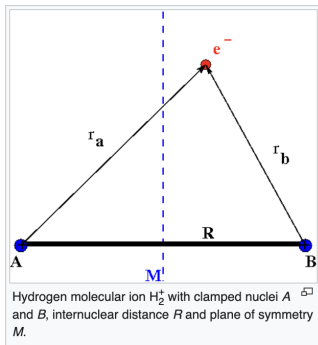
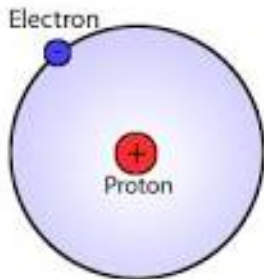
$$0 = 0 \quad (2)$$

- ▶ We will call this the first spherical harmonic:

$$\psi_{1,0,0}(\vec{r}) = \sqrt{\frac{1}{4\pi}} e^{-r}$$



- ▶ What can we determine from the picture?
- ▶ How many spin states do we need to describe this system?
- ▶ How many orbitals?



Ansatz for Spatial Component of Wavefunction of H_2^+

- ▶ The original Hamiltonian for H: $\hat{H} = -\frac{1}{2}\nabla_r - \frac{1}{r}$
- ▶ The new Hamiltonian for H_2^+ : $\hat{H} = -\frac{1}{2}\nabla_r - \frac{1}{|\vec{r}|} - \frac{1}{|\vec{r}-\vec{R}|}$
- ▶ Approximate the wavefunction as a linear combination of the 1s orbitals:

$$\psi(\vec{r}) \approx c_1\psi_{1,0,0} + c_2\psi_{1,0,0}(\vec{r} - \vec{R})$$

- ▶ Since the vector span $\{\psi_{1,0,0}(\vec{r}), \psi_{1,0,0}(\vec{r} - \vec{R})\}$ is isomorphic to \mathbb{C}^2 , the hamiltonian can be approximated by a 2×2 matrix and solved with a Galerkin projection:

Galerkin Projection Continued

$$\begin{aligned}H\psi &= E\psi \\ \varepsilon &= \int \psi_{100}(\vec{r})(H\psi_{100}(\vec{r}))d\vec{r} \\ -t &= \int \psi_{100}(\vec{r})(H\psi_{100}(\vec{r} - \vec{R}))d\vec{r} \\ s &= \int \psi_{100}(\vec{r})\psi_{100}(\vec{r} - \vec{R})d\vec{r}\end{aligned}$$

- ▶ Using the Galerkin projection, we can write the generalized eigenvalue problem as:

$$\begin{pmatrix} \varepsilon & -t \\ -t & \varepsilon \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = E \begin{pmatrix} 1 & s \\ s & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} \quad (3)$$

- ▶ One finds that the eigenenergies are: $E_0 = \frac{\varepsilon-t}{1+s}$ and $E_e = \frac{\varepsilon+t}{1-s}$ with corresponding eigenvectors: $\vec{c}_0 = \frac{1}{\sqrt{2(1+s)}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$ and

$$\vec{c}_e = \frac{1}{\sqrt{2(1-s)}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Identical Particles

- ▶ wavefunction has spatial and spin components,
 $\Psi(x_1, x_2) \equiv \Psi((r_1, \sigma_1), (r_2, \sigma_2))$
- ▶ The wavefunction for electrons is fermionic and is in the space
- ▶

The wavefunction $|\Psi\rangle$ for electrons is always a fermionic state and is in the space $\mathcal{A}_2 = \bigwedge^2 L^2(\mathbb{R}^3; \mathbb{C}^2)$, which consists of all anti-symmetric functions in the tensor product space $L^2(\mathbb{R}^3; \mathbb{C}^2) \otimes L^2(\mathbb{R}^3; \mathbb{C}^2)$.

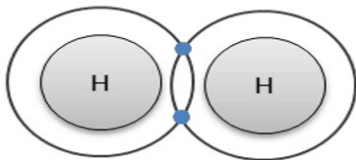
- ▶ Because the Hamiltonian doesn't depend on spin, we have
 $[(S^{tot})^2, H] = 0$ and $[(S_z^{tot}), H]$
- ▶ We can separate spin and spatial degrees of freedom
- ▶ Additionally, if we have a triplet state, the spatial part of the wavefunction must be anti-symmetric

$$\varphi(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}(\phi_1(\vec{r}_1)\phi_2(\vec{r}_1) - \phi_1(\vec{r}_2)\phi_2(\vec{r}_1))$$

H_2 Molecule

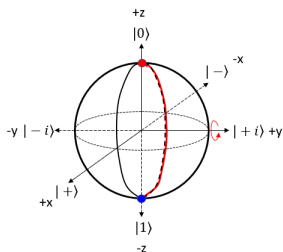
- ▶ What do we need to account for the extra electron?

Covalent bond - H_2

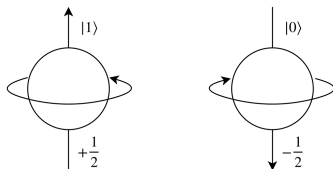


Two Spin 1/2 Particles

- ▶ Spin basis states for a system of one spin $\frac{1}{2}$ particles
 - ▶ $|+z\rangle, |-z\rangle$



- ▶ Spin basis states for a system of two spin $\frac{1}{2}$ particles
 - $|+z, +z\rangle, |+z, -z\rangle, |-z, +z\rangle, |-z, -z\rangle$
 - ▶ $|+z, -z\rangle$



Two Spin 1/2 Particles Generators of Rotation

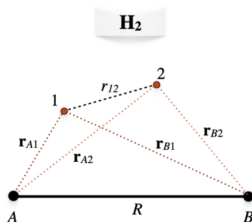
- ▶ Angular Momentum Operators: $\hat{S}_1 = \hat{S}_{1x} + \hat{S}_{1y} + \hat{S}_{1z}$
 - ▶ Angular Momentum : $[\hat{S}_1, \hat{S}_2] = 0$
- ▶ As Tim touched upon, the eigenfunctions collapse to an eigenstate upon measurement.
 - ▶ If +z is measured for the first particle, we can label $S_{1z} = \frac{\hbar}{2}$.
 - ▶ If -z is measured for the second particle, we can label $S_{2z} = -\frac{\hbar}{2}$.

Two Spin 1/2 Particles Generators of Rotation

- ▶ This state we just discussed is represented as
$$|+z, -z\rangle = |+z\rangle_1 \otimes |-z\rangle_2$$
 - ▶ Number of spin states for spin 1/2 particles $N = 2^n$ where n is the number of particles.
- ▶ Total Z-Spin is $S_z = -\frac{\hbar^2}{2^2}$

H₂ Molecule

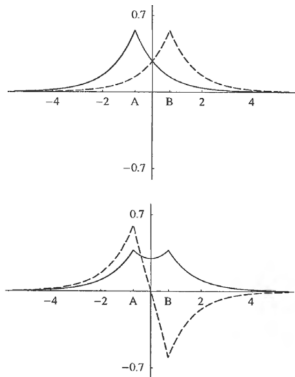
- ▶ The Geometry of our System:



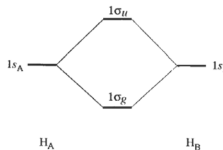
- ▶ Both electrons occupy the 1s orbital
- ▶ Spatial wavefunctions:

$$\phi_1(\vec{r}) = \frac{1}{\sqrt{2(1+s)}} [\psi_{100}(\vec{r}_{A1}) + \psi_{100}(\vec{r}_{B2})]$$
$$\phi_2(\vec{r}) = \frac{1}{\sqrt{2(1-s)}} [\psi_{100}(\vec{r}_A) - \psi_{100}(\vec{r}_{B2})]$$

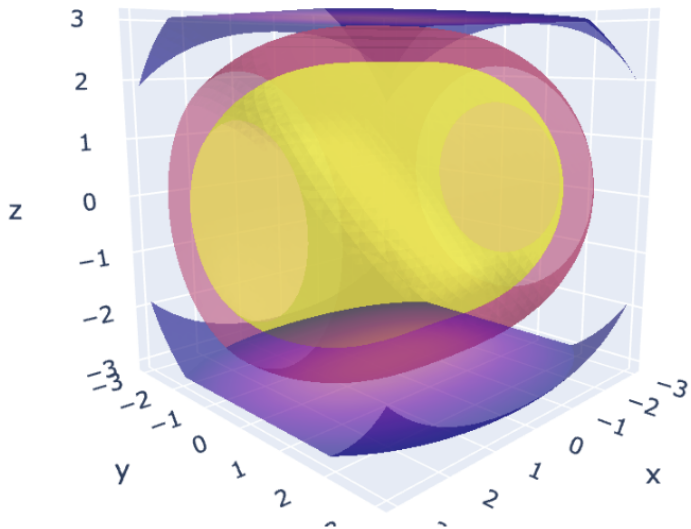
Ground State Antibonding and Bonding



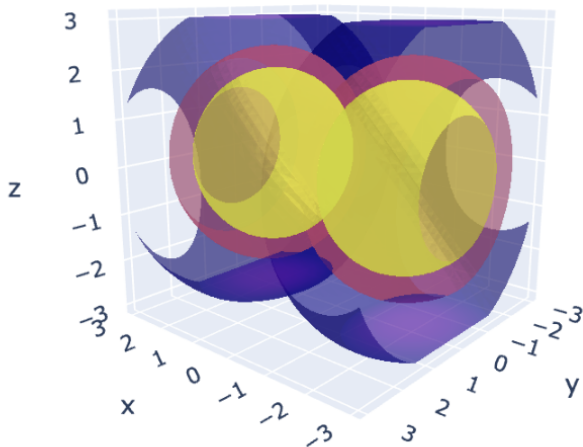
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Ground State Antibonding and Bonding



Ground State Antibonding and Bonding



N-particles

- ▶ $\Psi(x_1, \dots, x_N) \in \otimes^N L^2(\mathbb{R}^3; \mathbb{C}^2)$
- ▶ Permutation Operator- the operator that exchanges particles eigenvalues have to be ± 1
- ▶ $P(i, j)\Psi_F(x_1, \dots, x_i, \dots, x_j, \dots, x_N) = \Psi_F(x_1, \dots, x_j, \dots, x_i, \dots, x_N)$
- ▶ The symmetric group has $N!$ permutations
$$C_F \sum_{\pi \in \text{Sym}(N)} (-1)^\pi \psi_{\pi(1)}(x_1) \psi_{\pi(2)}(x_2) \dots \psi_{\pi(N)}(x_N)$$
- ▶ $(-1)^\pi = \begin{cases} 1 & \pi(\text{even}) \\ -1 & \pi(\text{odd}) \end{cases}$
- ▶ Simplest for $N = 2$

$$\mathcal{A}_N := \bigwedge^N L^2(\mathbb{R}^3; \mathbb{C}^2) \subset \bigotimes^N L^2(\mathbb{R}^3; \mathbb{C}^2).$$

Slater Determinant

- ▶ rows \rightarrow electrons
- ▶ columns \rightarrow spin orbitals
- ▶ The Slater determinant is given by:

$$\Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_1(1) & \chi_2(1) & \cdots & \chi_N(1) \\ \chi_1(2) & \chi_2(2) & \cdots & \chi_N(2) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_1(N) & \chi_2(N) & \cdots & \chi_N(N) \end{vmatrix}$$

Hartree-Fock Theory

- ▶ Hartree-Fock takes \mathcal{A}_N and assumes that the wavefunction is a single Slater determinant

- ▶ Variational Principle (Rayleigh-Ritz Method) where

$$E_\psi = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

- ▶ $\frac{\partial E_\psi}{\partial \psi} [\psi_*] = 0$

- ▶ This becomes a minimization problem:

$$E_{HF} = \min_{\psi \in \mathcal{A}_N^0, \langle \psi | \psi \rangle = 1} \langle \Psi | H | \Psi \rangle, \text{ where } \mathcal{A}_N^0 \text{ is the set of all Slater determinants for } N \text{ electrons}$$

Hartree-Fock on the Molecular Hamiltonian

$$H = \sum_{i=1}^N -\frac{1}{2}\Delta_{r_i} - \sum_{i=1}^N \frac{Z_i}{|r_j - R_j|} + \sum_{i < j}^N \frac{1}{|r_i - r_j|}$$

- ▶ The scaling of hartree fock

$$\langle \Psi | \sum_{i=1}^N \left(-\frac{1}{2}\nabla_{r_i} + V_{\text{ext}}(r_i) \right) | \Psi \rangle = N \langle \Psi | -\frac{1}{2}\nabla_{r_1} + V_{\text{ext}}(r_1) | \Psi \rangle \quad (4)$$

$$\langle \Psi | \sum_{i < j} \frac{1}{|r_i - r_j|} | \Psi \rangle = \binom{N}{2} \langle \Psi | \frac{1}{|r_1 - r_2|} | \Psi \rangle \quad (5)$$

Hartree Fock Continued

- ▶ There is only one interacting term with the Hamiltonian in the computation

$$\begin{aligned} & \langle \Psi | -\frac{1}{2}\Delta_{\mathbf{r}_1} + V_{\text{ext}}(\mathbf{r}_1) | \Psi \rangle \\ &= \frac{1}{N!} \sum_{\pi, \pi'} (-1)^\pi (-1)^{\pi'} \langle \psi_{\pi(1)}(\mathbf{x}_1) | -\frac{1}{2}\Delta_{\mathbf{r}_1} + V_{\text{ext}}(\mathbf{r}_1) | \psi_{\pi'(1)}(\mathbf{x}_1) \rangle_{\mathbf{x}_1} \\ & \quad \times \prod_{k=2}^N \langle \psi_{\pi(k)}(\mathbf{x}_k) | \psi_{\pi'(k)}(\mathbf{x}_k) \rangle_{\mathbf{x}_k} \\ &= \frac{1}{N!} \sum_{\pi, \pi'} (-1)^\pi (-1)^{\pi'} \langle \psi_{\pi(1)}(\mathbf{x}_1) | -\frac{1}{2}\Delta_{\mathbf{r}_1} + V_{\text{ext}}(\mathbf{r}_1) | \psi_{\pi'(1)}(\mathbf{x}_1) \rangle_{\mathbf{x}_1} \prod_{k=2}^N \delta_{\pi(k)\pi'(k)} \end{aligned}$$

- ▶ The contribution of this term is zero unless $\pi(k) = \pi'(k)$
- ▶ Therefore: $\langle \Psi | 1_{\text{body}} | \Psi \rangle = \frac{1}{N} \sum_{i=1}^N \langle \psi_i | -\frac{1}{2}\nabla + V_{\text{ext}} | \psi_i \rangle$

Two Body Term



$$\begin{aligned} & \langle \Psi | \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} | \Psi \rangle \\ &= \frac{1}{N!} \sum_{\pi, \pi'} (-1)^\pi (-1)^{\pi'} \left\langle \psi_{\pi(1)}(\mathbf{x}_1) \psi_{\pi(2)}(\mathbf{x}_2) \left| \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \psi_{\pi'(1)}(\mathbf{x}_1) \psi_{\pi'(2)}(\mathbf{x}_2) \right\rangle_{\mathbf{x}_1, \mathbf{x}_2} \\ & \quad \times \prod_{k=3}^N \left\langle \psi_{\pi(k)}(\mathbf{x}_k) \left| \psi_{\pi'(k)}(\mathbf{x}_k) \right\rangle_{\mathbf{x}_k} \\ &= \frac{1}{N!} \sum_{\pi, \pi'} (-1)^\pi (-1)^{\pi'} \left\langle \psi_{\pi(1)}(\mathbf{x}) \psi_{\pi(2)}(\mathbf{x}') \left| \frac{1}{|\mathbf{r} - \mathbf{r}'|} \right| \psi_{\pi'(1)}(\mathbf{x}) \psi_{\pi'(2)}(\mathbf{x}') \right\rangle_{\mathbf{x}, \mathbf{x}'} \\ & \quad \times \prod_{k=3}^N \delta_{\pi(k)\pi'(k)}. \end{aligned}$$

We will see that when $\pi(1) = \pi'(1)$ we get $(-1)(-1) = 1$ and when $\pi(1) = \pi'(2)$ we obtain $(-1)(1) = 1$. The two permutations when this term is non-zero are when:

$$\pi(1) = \pi'(1) = i, \quad \pi(2) = \pi'(2) = j$$



$$\pi(1) = \pi'(2) = i, \quad \pi(2) = \pi'(1) = j,$$

Simplifying 2-body term

$$\begin{aligned} & \langle \Psi | \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle \\ &= \frac{1}{2} \sum_{i \neq j}^N \left(\langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') \rangle - \langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_j(\mathbf{x}) \psi_i(\mathbf{x}') \rangle \right) \\ &= \frac{1}{2} \sum_{i,j}^N \left(\langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') \rangle - \langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_j(\mathbf{x}) \psi_i(\mathbf{x}') \rangle \right). \end{aligned}$$

Hartree Fock Energy Functional

$$\begin{aligned} & \langle \Psi | \sum_{i < j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} | \Psi \rangle \\ &= \frac{1}{2} \sum_{i \neq j}^N \left(\langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') \rangle - \langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_j(\mathbf{x}) \psi_i(\mathbf{x}') \rangle \right) \\ &= \frac{1}{2} \sum_{i,j}^N \left(\langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') \rangle - \langle \psi_i(\mathbf{x}) \psi_j(\mathbf{x}') | \frac{1}{|\mathbf{r} - \mathbf{r}'|} | \psi_j(\mathbf{x}) \psi_i(\mathbf{x}') \rangle \right). \end{aligned}$$