Quantum Mechanics II

Lots of Identical Particles (2)

The Hartree-Fock Method

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Pink Floyd: "Another Brick in the Wall (Pt. II)"

Lots of Identical Particles (2)

The Hartree-Fock Method

- The story so far…
- N-fermion systems represented as

$$|\Psi\rangle_F = \hat{c}^\dagger_\alpha \hat{c}^\dagger_\beta \cdots \hat{c}^\dagger_\gamma \cdots |\mathbf{0}\rangle_F = |\alpha\beta\cdots\gamma\cdots\rangle_F$$

$$= -|\beta\alpha\cdots\gamma\cdots\rangle = -|\gamma\beta\cdots\alpha\cdots\rangle$$

antisymmetric by construction

$$\{\hat{c}_\alpha, \hat{c}_\beta\} = 0 = \{\hat{c}^\dagger_\alpha, \hat{c}^\dagger_\beta\} \qquad \{\hat{c}_\alpha, \hat{c}^\dagger_\beta\} = \delta_{\alpha,\beta}\mathbb{1}$$

- The basis of 1-particle states

$$|\alpha\rangle_F := \hat{c}^\dagger_\alpha |\mathbf{0}\rangle_F$$

may well include the effect of external fields

- …may be transformed by a unitary transformation

$$\xrightarrow{\text{H-F}} \quad |\phi_\alpha\rangle := \mathbb{U}_\alpha{}^\beta\,|\beta\rangle$$

effect of external fields as well as antisymmetrization

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The Hartree-Fock Method

- For a unitary transformation $|\alpha\rangle_F \xrightarrow{\text{H-F}} |\phi_\alpha\rangle := \mathbb{U}_\alpha{}^\beta\,|\beta\rangle$

$$\mathbb{U}^\dagger = \mathbb{U}^{-1} \qquad \mathbb{U}_\alpha{}^\beta = [e^{i\boldsymbol{\eta}}]_\alpha{}^\beta = \delta_\alpha{}^\beta + i\eta_\alpha{}^\beta + \ldots \qquad [\eta_\alpha{}^\beta]^\dagger = [\eta_\alpha{}^\beta]$$

- Correspondingly,

$$\hat{c}^\dagger_\alpha \to \hat{c}^\dagger_\alpha + i\eta_\alpha{}^\beta\,\hat{c}^\dagger_\beta + \ldots$$

- …and calculate precisely to 1st order in $\boldsymbol{\eta}$:

$$|\Psi\rangle_F \to |\Psi\rangle_F + |\delta\Psi\rangle_F + \mathscr{O}(\boldsymbol{\eta}^2)$$

$$|\delta\Psi\rangle := \Big(|\Psi\rangle_F\Big)_{\hat{c}^\dagger \to i\boldsymbol{\eta}\cdot\hat{c}^\dagger} = i\sum_{\text{“}\alpha\in\Psi\text{”}} \eta_\alpha{}^\beta\hat{c}^\dagger_\beta\hat{c}_\alpha\,|\Psi\rangle_F = i\sum_\beta\sum_{\text{“}\alpha\in\Psi\text{”}} |\Psi\rangle_{\beta\alpha}$$

move from α to β

- Notice:

$$\underbrace{\eta_\alpha{}^\beta\hat{c}^\dagger_\beta\hat{c}_\alpha\,|\Psi\rangle_F}_{\text{no summation}} \equiv 0 \quad \text{if “}\alpha\notin\Psi\text{”}: \ \text{then } \hat{c}_\alpha\,|\Psi\rangle_F \equiv 0$$

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The Hartree-Fock Method

- Operators in the "1-particle basis"
- "Additive 1-particle operators"

$$\widehat{R}_{(1)} = \sum_i \widehat{R}(\vec{r}_i) = \sum_{\alpha,\beta} \langle\alpha|\widehat{R}_{(1)}|\beta\rangle\, \hat{c}^\dagger_\alpha\, \hat{c}_\beta = \sum_{\alpha,\beta} R_{\alpha,\beta}\, \hat{c}^\dagger_\alpha\, \hat{c}_\beta$$

single-particle position

- "Additive 2-particle (pair-)operators"

$$\widehat{R}_{(2)} = \tfrac{1}{2}\sum_{i\neq j} \widehat{R}(\vec{r}_i,\vec{r}_j) = \sum_{\alpha,\beta,\gamma,\delta} R_{\alpha\beta,\gamma\delta}\, \hat{c}^\dagger_\alpha\, \hat{c}^\dagger_\beta\, \hat{c}_\gamma\, \hat{c}_\delta$$

pair-wise interaction

$$R_{\alpha\beta,\gamma\delta} := \int d^3\vec{r}_1 \int d^3\vec{r}_2\, \langle\alpha|\vec{r}_1\rangle\langle\beta|\vec{r}_2\rangle\widehat{R}(\vec{r}_1,\vec{r}_2)\langle\vec{r}_1|\gamma\rangle\langle\vec{r}_2|\delta\rangle$$

$$:= \int d^3\vec{r}_1 \int d^3\vec{r}_2\, \psi^*_\alpha(\vec{r}_1)\psi^*_\beta(\vec{r}_2)\widehat{R}(\vec{r}_1,\vec{r}_2)\psi_\gamma(\vec{r}_1)\psi_\delta(\vec{r}_2)$$

Lots of Identical Particles (2)

The Hartree-Fock Method

- Calculate the energy, by varying the states

$$|\delta\Psi\rangle = i \sum_{\text{“}\alpha\in\Psi\text{”}} \eta_\alpha{}^\beta \hat{c}^\dagger_\beta \hat{c}_\alpha |\Psi\rangle_F = i \sum_\beta \sum_{\text{“}\alpha\in\Psi\text{”}} |\Psi\rangle_{\beta\alpha}$$

- Useful:

$$\begin{aligned} \langle \hat{c}^\dagger_\alpha \hat{c}_\alpha \rangle_\Psi &= 1 \;\&\; \langle \hat{c}_\alpha \hat{c}^\dagger_\alpha \rangle_\Psi = 0 \quad \text{if “}\alpha \in \Psi\text{”} \\ \langle \hat{c}^\dagger_\beta \hat{c}_\beta \rangle_\Psi &= 0 \;\&\; \langle \hat{c}_\beta \hat{c}^\dagger_\beta \rangle_\Psi = 1 \quad \text{if “}\beta \notin \Psi\text{”} \end{aligned}$$

- Up to pair-wise interactions

$$\widehat{H} = \sum_{\alpha,\beta} T_{\alpha,\beta} \hat{c}^\dagger_\alpha \hat{c}_\beta + \tfrac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} V_{\alpha\beta,\gamma\delta} \hat{c}^\dagger_\alpha \hat{c}^\dagger_\beta \hat{c}_\gamma \hat{c}_\delta$$

- Then

$$0 \stackrel{!}{=} \langle \Psi | \widehat{H} | \delta\Psi \rangle_{\beta\alpha} = T_{\alpha\beta} + \underbrace{\sum_{\text{“}\gamma\in\Psi\text{”}} (V_{\alpha\gamma,\beta\gamma} - V_{\alpha\gamma,\gamma\beta})}_{\text{effectively a 1-particle operator} \;:=\; V^{\text{H-F}}_{\alpha,\beta}} \qquad \text{“}\alpha \in \Psi \not\ni \beta\text{”}$$

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The Hartree-Fock Method

$$0 \stackrel{!}{=} \langle\Psi|\widehat{H}|\delta\Psi\rangle_{\beta\alpha} = T_{\alpha\beta} + \sum_{\text{“}\gamma\in\Psi\text{”}} (V_{\alpha\gamma,\beta\gamma} - V_{\alpha\gamma,\gamma\beta})$$

- Define the Hartree-Fock (approximation to the) Hamiltonian

$$\widehat{H}^{\text{H-F}}_{\alpha,\beta} := T_{\alpha,\beta} + V^{\text{H-F}}_{\alpha,\beta} = T_{\alpha,\beta} + \sum_{\text{“}\gamma\in\Psi\text{”}} (V_{\alpha\gamma,\beta\gamma} - V_{\alpha\gamma,\gamma\beta})$$

- Find its eigenvalues, *i.e.*, diagonalize it

$$\epsilon_\alpha : \quad \mathbb{H}^{\text{H-F}}\,|\epsilon_\alpha\rangle = \epsilon_\alpha\,|\epsilon_\alpha\rangle \qquad \mathbb{H}^{\text{H-F}} \to \text{diag}(\epsilon_1, \epsilon_2, \cdots)$$

- The full energy is

$$E = \langle\Psi|\widehat{H}|\Psi\rangle = \sum_{\text{“}\alpha\in\Psi\text{”}} T_{\alpha,\alpha} + \tfrac{1}{2} \sum_{\text{“}\alpha,\beta\in\Psi\text{”}} (V_{\alpha\beta,\alpha\beta} - V_{\alpha\beta,\beta\alpha})$$

- while

$$\epsilon_\alpha = \langle\alpha|\widehat{H}^{\text{H-F}}|\alpha\rangle = T_{\alpha,\alpha} + \Big(V^{\text{H-F}}_{\alpha,\alpha} := \sum_{\text{“}\gamma\in\Psi\text{”}} (V_{\alpha\gamma,\alpha\gamma} - V_{\alpha\gamma,\gamma\alpha})\Big)$$

- so

$$E = \sum_{\text{“}\alpha\in\Psi\text{”}} \Big(\epsilon_\alpha - \tfrac{1}{2} V^{\text{H-F}}_{\alpha,\alpha}\Big)$$

← **Pretty neat!!**

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The Hartree-Fock Method

- Back, in the coordinate representation…

$$\psi_\alpha(\vec r) := \langle \vec r|\alpha\rangle = \langle \vec r|a,\sigma\rangle = \psi_{a,\sigma}(\vec r)$$

$$E = \sum_\alpha \int d^3\vec r\, \psi^*_\alpha(\vec r)\Big[-\frac{\hbar^2}{2M}\vec\nabla^2 + W(\vec r)\Big]\psi_\alpha(\vec r)$$

$$+\frac{1}{2}\sum_{\alpha\beta}\iint d^3\vec r_1 d^3\vec r_2\, \psi^*_\alpha(\vec r_1)\psi^*_\beta(\vec r_2)\,\widehat V(\vec r_1-\vec r_2)\,\psi_\alpha(\vec r_1)\psi_\beta(\vec r_2)$$

direct term

$$-\frac{1}{2}\sum_{\alpha\beta}\iint d^3\vec r_1 d^3\vec r_2\, \psi^*_\alpha(\vec r_1)\psi^*_\beta(\vec r_2)\,\widehat V(\vec r_1-\vec r_2)\,\psi_\beta(\vec r_1)\psi_\alpha(\vec r_2)$$

exchange term

- …with spin-independent pair-wise interaction

$$\widehat V(\vec r_1-\vec r_2) = V(\vec r_1-\vec r_2)\,\delta_{\sigma,\sigma'} \qquad \langle\delta\Psi|\widehat H|\Psi\rangle \stackrel{!}{=} 0$$

nonlinear integro-differential equation

$$\epsilon_a\,\psi_{a\,\sigma}(\vec r) = \Big[-\frac{\hbar^2}{2M}\vec\nabla^2 + W(\vec r) + V(\vec r;\psi)\Big]\psi_{a\,\sigma}(\vec r) - \sum_b V_{b\,a\,\sigma}(\vec r;\psi)\,\psi_{b\,\sigma}(\vec r)$$

$$V(\vec r;\psi) := \sum_{b\,\sigma'}\int d^3\vec r'\,|\psi_{b\,\sigma'}(\vec r')|^2 V(\vec r-\vec r') \qquad V_{b\,a\,\sigma}(\vec r;\psi) := \int d^3\vec r'\,\psi^*_{b\,\sigma}(\vec r')\,V(\vec r-\vec r')\,\psi_{a\,\sigma}(\vec r')$$

Quantum Mechanics II

Now, go forth and calculate!!

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