The Hartree-Fock Theory

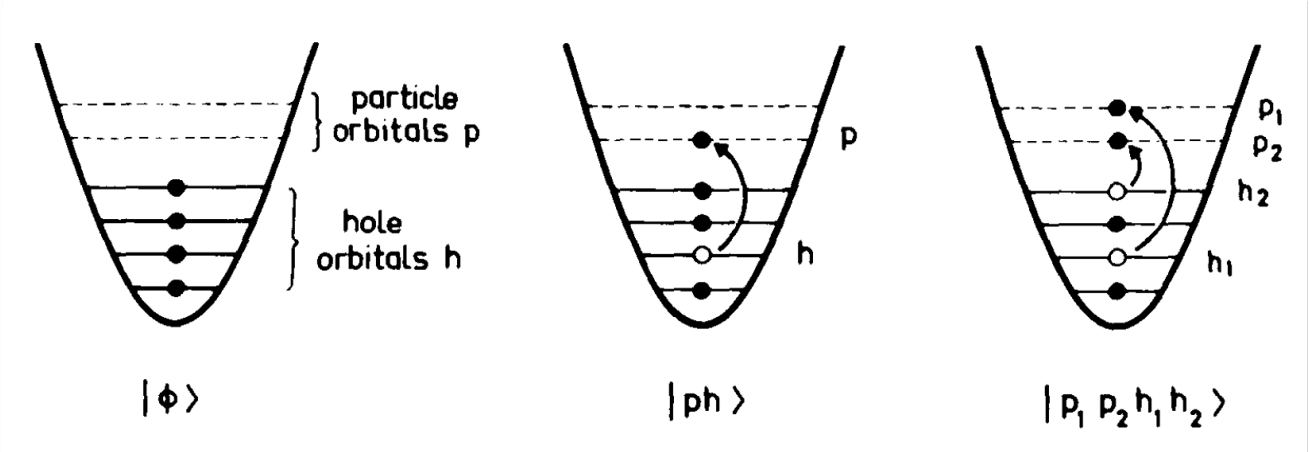
Jiangming Yao (尧江明)

中山大学物理与天文学院

Outline

Introduction

Introduction



- Configuration: the distribution of Fermions in orbitals. For the case of A Fermions,

$$\Phi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_A\right) = \frac{1}{\sqrt{A!}} \sum_{\pi} (-1)^{\pi} \prod_{k=1}^{A} \psi_k\left(\boldsymbol{r}_{k_\pi}\right)$$

  where π is a permutation of the indices $i = 1, \ldots, A$ and $(-1)^{\pi}$ is its sign, $+1$ for even and -1 for odd permutations. The permutation changes the index i into i_π.
- Wave function of a many-body Fermionic system:

$$\Psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_A) = \sum_i c_i \Phi_i\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_A\right).$$

A brief review of second quantization

Operators

- The one-body operator $\hat{F}$:

$$\hat{F} \equiv \sum_{k=1}^{A} \hat{f}(\mathbf{r}_k) = \sum_{\alpha\beta} f_{\alpha\beta} a_\alpha^\dagger a_\beta \equiv \sum_{\alpha\beta} f_{\alpha\beta} A_\beta^\alpha,$$

where the matrix element $f_{\alpha\beta}$ is defined as

$$f_{\alpha\beta} \equiv \langle\alpha|\hat{F}|\beta\rangle = \int d^3\mathbf{r}\psi_\alpha^*(\mathbf{r})\hat{f}\psi_\beta(\mathbf{r}).$$

- The two-body operator $\hat{V}$,

$$\hat{V} = \frac{1}{2}\sum_{k\neq k'} \hat{v}(\mathbf{r}_k, \mathbf{r}_{k'}) = \frac{1}{2}\sum_{ijkl} v_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \equiv \frac{1}{2}\sum_{ijkl} v_{ijkl} A_{kl}^{ij} = \frac{1}{4}\sum_{ijkl} \bar{v}_{ijkl} A_{kl}^{ij},$$

where the matrix element of v_{ijkl} is defined as

$$v_{ijkl} = \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \psi_i^*(\boldsymbol{r})\psi_j^*\left(\boldsymbol{r}'\right) \hat{v}\left(\boldsymbol{r}, \boldsymbol{r}'\right) \psi_k(\boldsymbol{r})\psi_l\left(\boldsymbol{r}'\right),$$

$$A_{kl}^{ij} = a_i^\dagger a_j^\dagger a_l a_k.$$

and $\bar{v}_{ijkl}$ is defined as

$$\bar{v}_{ijkl} \equiv v_{ijkl} - v_{ijlk}.$$

The Wick theorem

Normal-ordered (正规乘积) operators

- Anticommutation between Fermionic creation and annihilation operators:

$$\left\{a_i^\dagger, a_j^\dagger\right\} = \{a_i, a_j\} = 0, \quad \left\{a_i^\dagger, a_j\right\} = \delta_{ij}$$

  The indices are collective labels for the quantum numbers of single-particle states.

- A complete basis for a many-body Hilbert space,

$$|\Phi\{i_1 \ldots i_A\}\rangle = \prod_{k=1}^{A} a_{i_k}^\dagger |-\rangle$$

  which is a Slater determinant. Here we choose $|\Phi\rangle$ as the reference state with respect to which the operators will be normal-ordered.

- Define the normal-ordered operator

$$a_i^\dagger a_j \equiv \left\{a_i^\dagger a_j\right\} + \overbrace{a_i^\dagger a_j}$$

  where the brackets $\{\ldots\}$ indicate normal ordering, and the brace over a pair of creation and annihilation operators means that they have been contracted,

$$\overbrace{a_i^\dagger a_j} \equiv \langle\Phi \left| a_i^\dagger a_j \right| \Phi\rangle \equiv \rho_{ji}, \quad \langle\Phi|\{\cdots\}|\Phi\rangle = 0.$$

Normal-ordered (正规乘积) operators

Starting from the one-body case, we can define normal-ordered A-body operators recursively by evaluating all contractions between creation and annihilation operators, e.g.,

$$
\begin{aligned}
& a^\dagger_{i_1} \ldots a^\dagger_{i_A} a_{j_A} \ldots a_{j_1} \\
& \equiv \left\{ a^\dagger_{i_1} \ldots a^\dagger_{i_A} a_{j_A} \ldots a_{j_1} \right\} \\
& \quad + \overbrace{a^\dagger_{i_1} a_{j_1}} \left\{ a^\dagger_{i_2} \ldots a^\dagger_{i_A} a_{j_A} \ldots a_{j_2} \right\} - \overbrace{a^\dagger_{i_1} a_{j_2}} \left\{ a^\dagger_{i_2} \ldots a^\dagger_{i_A} a_{j_A} \ldots a_{j_3} a_{j_1} \right\} + \text{ singles} \\
& \quad + \left(\overbrace{a^\dagger_{i_1} a_{j_1}} \overbrace{a^\dagger_{i_2} a_{j_2}} - \overbrace{a^\dagger_{i_1} a_{j_2}} \overbrace{a^\dagger_{i_2} a_{j_1}} \right) \left\{ a^\dagger_{i_3} \ldots a^\dagger_{i_A} a_{j_A} \ldots a_{j_3} \right\} + \text{ doubles} \\
& \quad + \ldots + \text{ full contractions.}
\end{aligned}
$$

The two-body operator

$$
\begin{aligned}
a^\dagger_i a^\dagger_j a_l a_k = & \left\{ a^\dagger_i a^\dagger_j a_l a_k \right\} + \overbrace{a^\dagger_i a_k} \{ a^\dagger_j a_l \} + \overbrace{a^\dagger_j a_l} \{ a^\dagger_i a_k \} - \overbrace{a^\dagger_i a_l} \{ a^\dagger_j a_k \} - \overbrace{a^\dagger_j a_k} \{ a^\dagger_i a_l \} \\
& + \overbrace{a^\dagger_i a_k} \overbrace{a^\dagger_j a_l} - \overbrace{a^\dagger_i a_l} \overbrace{a^\dagger_j a_k}.
\end{aligned}
$$

Normal-ordered (正规乘积) operators

An important property is that we can freely anticommute creation and annihilation operators within a normal-ordered string

$$\left\{\ldots a_i^\dagger a_j \ldots\right\} = -\left\{\ldots a_j a_i^\dagger \ldots\right\}$$

Normal-ordered (正规乘积) operators

The product of two norm-ordered operators can be expanded with the help of Wick theorem:

$$\begin{aligned}
&\left\{a_{i_1}^\dagger \dots a_{i_N}^\dagger a_{j_N} \dots a_{j_1}\right\}\left\{a_{k_1}^\dagger \dots a_{k_M}^\dagger a_{l_M} \dots a_{l_1}\right\} \\
&= (-1)^{M\cdot N}\left\{a_{i_1}^\dagger \dots a_{i_N}^\dagger a_{k_1}^\dagger \dots a_{k_M}^\dagger a_{j_N} \dots a_{j_1} a_{l_M} \dots a_{l_1}\right\} \\
&\quad +(-1)^{M\cdot N} \overbrace{a_{i_1}^\dagger a_{l_1}} \left\{a_{i_2}^\dagger \dots a_{k_M}^\dagger a_{j_N} \dots a_{l_2}\right\} \\
&\quad +(-1)^{(M-1)(N-1)} \overbrace{a_{j_N} a_{k_1}^\dagger} \left\{a_{i_1}^\dagger \dots a_{k_M}^\dagger a_{j_N} \dots a_{j_2}\right\} \\
&\quad + \text{singles} + \text{doubles} + \dots .
\end{aligned}$$

The phase factors appear because we anti-commute the creators and annihilators until they are grouped in the canonical order, i.e., all $a^\dagger$ appear to the left of the a. In the process, we also encounter a new type of contraction,

$$\overbrace{a_i a_j^\dagger} \equiv \left\langle \Phi \left| a_i a_j^\dagger \right| \Phi \right\rangle = \left\langle \Phi \left| \delta_{ij} - a_j^\dagger a_i \right| \Phi \right\rangle = \delta_{ij} - \rho_{ij} \equiv \bar{\rho}_{ij}$$

as expected from the canonical anti-commutator algebra. $\bar{\rho}$ is the so-called hole density matrix.

Normal-ordered (正规乘积) operators

Generally, one has the following relations for arbitrary reference states,

$$\left\{A^{a[b]}_{cd}\right\}\left\{A^{ij}_{[k]l}\right\} = -\lambda^b_k\left\{A^{aij}_{cdl}\right\} + \cdots$$
$$\left\{A^{ab}_{[c]d}\right\}\left\{A^{i[j]}_{kl}\right\} = -\xi^j_c\left\{A^{abi}_{dkl}\right\} + \cdots$$

where in canonical basis

$$\lambda^a_k = \delta^a_k n_a, \quad \xi^j_c = \lambda^j_c - \delta_{jc} = (n_j - 1)\delta_{jc} \equiv -\bar{n}_j\delta_{jc} = -\bar{\rho}_{cj}$$

- 1B1B:

$$\begin{aligned}\{a^\dagger_i a_j\}\{a^\dagger_k a_l\} &= -\{a^\dagger_i a^\dagger_k a_j a_l\} - \overbrace{a^\dagger_i a_l}\{a^\dagger_k a_j\} + \overbrace{a_j a^\dagger_k}\{a^\dagger_i a_j\} + \overbrace{a^\dagger_i a_l}\overbrace{a_j a^\dagger_k} \\ &= \{a^\dagger_i a^\dagger_k a_l a_j\} - \delta_{il}n_i\{a^\dagger_k a_j\} + \bar{n}_j\delta_{jk}\{a^\dagger_i a_j\} + n_i\bar{n}_j\delta_{il}\delta_{jk}. \quad (1)\end{aligned}$$

For short,

$$\{A^i_j\}\{A^k_l\} = \{A^{ik}_{jl}\} - \delta_{il}n_i\{A^k_j\} + \bar{n}_j\delta_{jk}\{A^i_j\} + n_i\bar{n}_j\delta_{il}\delta_{jk}. \quad (2)$$

Normal-ordered (正规乘积) operators

Generally, one has the following relations for arbitrary reference states,

$$\left\{A^{a[b]}_{cd}\right\}\left\{A^{ij}_{[k]l}\right\} = -\lambda^b_k\left\{A^{aij}_{cdl}\right\} + \cdots$$
$$\left\{A^{ab}_{[c]d}\right\}\left\{A^{i[j]}_{kl}\right\} = -\xi^j_c\left\{A^{abi}_{dkl}\right\} + \cdots$$

where the sign is determined by the number of permutations. The λ and ξ in canonical basis are defined as

$$\lambda^a_k = \rho^a_k = \delta^a_k n_a, \quad \xi^j_c = \lambda^j_c - \delta_{jc} = (n_j - 1)\delta_{jc} \equiv -\bar{n}_j\delta_{jc} = -\bar{\rho}_{cj}$$

- 1B2B:

$$\begin{aligned}
\{A^a_b\}\{A^{kl}_{mn}\} &= \{A^{akl}_{bmn}\} + (1-\hat{P}_{mn})\lambda^a_n\{A^{kl}_{bm}\} + (1-\hat{P}_{kl})\xi^l_b\{A^{ak}_{mn}\} \\
&\quad +(1-\hat{P}_{mn})(1-\hat{P}_{kl})\lambda^a_m\xi^l_b\{A^k_n\} \\
&= \{A^{akl}_{bmn}\} + (1-\hat{P}_{mn})n_a\delta_{an}\{A^{kl}_{bm}\} - (1-\hat{P}_{kl})\bar{n}_b\delta_{lb}\{A^{ak}_{mn}\} \\
&\quad -(1-\hat{P}_{mn})(1-\hat{P}_{kl})n_a\bar{n}_b\delta_{am}\delta_{lb}\{A^k_n\}. \qquad (3)
\end{aligned}$$

Normal-ordered (正规乘积) operators

A product of normal-ordered M and N-body operators has the general form

$$\hat{A}^{[M]}\hat{B}^{[N]} = \sum_{k=|M-N|}^{M+N} \hat{C}^{[k]}$$

Note that zero-body contributions, i.e., plain numbers, can only be generated if both operators have the same particle rank.

M. Hjorth-Jensen et al., An advanced course in computational nuclear physics, Lecture notes in Physics, 2017

Normal-ordered (正规乘积) operators

The commutator between two normal-ordered operators

$$\begin{aligned}\left[\left\{A^{ab}_{cd}\right\},\left\{A^{ij}_{kl}\right\}\right] &= \left\{A^{a[b]}_{cd}\right\}\left\{A^{ij}_{[k]l}\right\} - \left\{A^{ij}_{[k]l}\right\}\left\{A^{a[b]}_{cd}\right\} \\ &= -\lambda^b_k\left\{A^{aij}_{cdl}\right\} + \xi^b_k\left\{A^{aij}_{cdl}\right\} + \cdots \\ &= -\delta_{bk}\left\{A^{aij}_{cdl}\right\} + \cdots,\end{aligned}$$

where

$$\lambda^b_k - \xi^b_k = \delta_{bk}.$$

- 1B1B:

$$[\{A^a_b\},\{A^k_l\}] = -\delta_{al}\{A^k_b\} + \delta_{bk}\{A^a_l\} + (n_a\bar{n}_b - \bar{n}_a n_b)\delta_{al}\delta_{bk}. \tag{4}$$

where

$$(n_a\bar{n}_b - \bar{n}_a n_b) = n_a(1-n_b) - (1-n_a)n_b = n_a - n_b.$$

Normal-ordered (正规乘积) operators

The commutator between two normal-ordered operators

$$\begin{aligned}\left[\left\{A_{cd}^{ab}\right\},\left\{A_{kl}^{ij}\right\}\right] &= \left\{A_{cd}^{a[b]}\right\}\left\{A_{[k]l}^{ij}\right\}-\left\{A_{[k]l}^{ij}\right\}\left\{A_{cd}^{a[b]}\right\}\\ &= -\lambda_k^b\left\{A_{cdl}^{aij}\right\}+\xi_k^b\left\{A_{cdl}^{aij}\right\}+\cdots\\ &= -\delta_{bk}\left\{A_{cdl}^{aij}\right\}+\cdots,\end{aligned}$$

where

$$\lambda_k^b-\xi_k^b=\delta_{bk}.$$

- 1B2B:

$$\begin{aligned}[\{A_b^a\},\{A_{mn}^{kl}\}] &= -(1-\hat{P}_{mn})\delta_{am}\{A_{bn}^{kl}\}+(1-\hat{P}_{kl})\delta_{bk}\{A_{mn}^{al}\}\\ &\quad +(1-\hat{P}_{kl})(1-\hat{P}_{mn})(n_a-n_b)\delta_{an}\delta_{bl}\{A_m^k\}. \qquad (5)\end{aligned}$$

The variational principle

The variational principle

- Assuming $|\Psi_k\rangle$s are a set of eigenfunctions of the Hamiltonian H,

$$\hat{H}|\Psi_k\rangle = E_k|\Psi_k\rangle.$$

  All the $|\Psi_k\rangle$s span the Hilbert space and $\langle\Psi_k|\Psi_{k'}\rangle = \delta_{kk'}$.
- Any function $|\Phi\rangle$ certainty can be expanded in terms of $|\Psi_k\rangle$s,

$$|\Phi\rangle = \sum_k c_k|\Psi_k\rangle, \quad \sum_k |c_k|^2 = 1.$$

  where $k = 0, 1, 2, \cdots$ ordered in ascending energy.
- The energy expectation value of the Hamiltonian

$$\begin{aligned}\langle\Phi|\hat{H}|\Phi\rangle = \sum_{k=0}^{\infty}|c_k|^2E_k &= |c_0|^2E_0 + \sum_{k=1}^{\infty}|c_k|^2E_k \\ &= E_0(1 - \sum_{k=1}^{\infty}|c_k|^2) + \sum_{k=1}^{\infty}|c_k|^2E_k \\ &= E_0 + \sum_{k=1}^{\infty}|c_k|^2(E_k - E_0) \geq E_0\end{aligned}$$

The variational principle

- Only in the case that $c_0 = 1$ and $c_{k>0} = 0$, i.e,

$$|\Phi\rangle = |\Psi_0\rangle$$

the energy expectation value of the Hamiltonian is E_0.
In other words, the ground state wave function is obtained when the energy expectation value of the Hamiltonian takes the lowest value,

$$\delta\langle\Phi|\hat{H}|\Phi\rangle = 0, \quad \langle\Phi|\Phi\rangle = 1$$

which is equivalent to the following equation

$$\langle\delta\Phi|\hat{H}|\Phi\rangle - \lambda\langle\delta\Phi|\Phi\rangle = 0.$$

If $\langle\delta\Phi|$ is an arbitrary vector, one recovers the Schoerdinger equation,

$$\hat{H}|\Phi\rangle - \lambda|\Phi\rangle = 0.$$

In practical calculations, approximation is employed while constructing the trial wave function $|\Phi\rangle$. In this case, the trial wave function is not arbitrary. The variational principle cannot lead to the exact ground-state eigenfunction $|\Psi_0\rangle$ of the $\hat{H}$.

The HF approximation

The HF equation

- The Hartree-Fock approximation: the wave function of A-body systems is approximated as a Slater determinant,

$$|\Phi\rangle = \prod_{i=1}^{A} a_i^\dagger |-\rangle.$$

- Let's consider a Hamiltonian composed of one-body kinetic energy term and two-body interaction operators

$$\begin{aligned}\hat{H} &= \sum_{k_1 k_2} t_{k_2}^{k_1} A_{k_2}^{k_1} + \frac{1}{4} \sum_{k_1 k_2 k_3 k_4} \bar{v}_{k_3 k_4}^{k_1 k_2} A_{k_3 k_4}^{k_1 k_2} \\ &= E_0 + \sum_{k_1 k_2} f_{k_2}^{k_1} \{A_{k_2}^{k_1}\} + \frac{1}{4} \sum_{k_1 k_2 k_3 k_4} \Gamma_{k_3 k_4}^{k_1 k_2} \{A_{k_3 k_4}^{k_1 k_2}\},\end{aligned}$$

where according to the Wick theorem,

$$\begin{aligned}A_{k_2}^{k_1} &= \{A_{k_2}^{k_1}\} + \langle\Phi|A_{k_2}^{k_1}|\Phi\rangle, \\ A_{k_3 k_4}^{k_1 k_2} &= \{A_{k_3 k_4}^{k_1 k_2}\} + (1-\hat{P}_{12})(1-\hat{P}_{34})\{A_{k_3}^{k_1}\}\langle\Phi|A_{k_4}^{k_2}|\Phi\rangle + (1-\hat{P}_{34})\langle\Phi|A_{k_3}^{k_1}|\Phi\rangle\langle\Phi|A_{k_4}^{k_2}|\Phi\rangle\end{aligned}$$

The HF equation

The Hamiltonian is rewritten in terms of the normal-ordered operators (Homework: prove the below relation using the Wick theorem)

$$\hat{H} = E_0 + \sum_{k_1 k_3} f_{k_3}^{k_1} \{A_{k_3}^{k_1}\} + \frac{1}{4} \sum_{k_1 k_2 k_3 k_4} \Gamma_{k_3 k_4}^{k_1 k_2} \{A_{k_3 k_4}^{k_1 k_2}\},$$

where

$$\begin{aligned} E_0 &= \langle \Phi | \hat{H} | \Phi \rangle \\ &= \sum_{k_1 k_2} t_{k_2}^{k_1} \rho_{k_2}^{k_1} + \frac{1}{2} \sum_{k_1 k_2 k_3 k_4} \bar{v}_{k_3 k_4}^{k_1 k_2} \rho_{k_3}^{k_1} \rho_{k_4}^{k_2}, \\ f_{k_3}^{k_1} &= t_{k_3}^{k_1} + \sum_{k_2 k_4} \bar{v}_{k_3 k_4}^{k_1 k_2} \rho_{k_4}^{k_2}, \\ \Gamma_{k_3 k_4}^{k_1 k_2} &= \bar{v}_{k_3 k_4}^{k_1 k_2}. \end{aligned}$$

and we define the density matrix element

$$\rho_{k_4}^{k_2} = \langle \Phi | A_{k_4}^{k_2} | \Phi \rangle.$$

The HF equation

- The derivation of HF equation: basis transformation

$$\sum_{kl} f_l^k \{A_l^k\} = \sum_{k'l'} f_{l'}^{k'} \{A_{l'}^{k'}\},$$

where the matrix element $f_{l'}^{k'}$ is the matrix element of the one-body operator in a new (a.k.a. canonical) basis and it has a diagonal form,

$$f_{l'}^{k'} = \varepsilon_{k'} \delta_{l'}^{k'}.$$

In other words, there is a unitary transformation U, which diagonalizes the one-body matrix F,

$$U^\dagger F U = \mathrm{diag}(\varepsilon_1, \varepsilon_2, \cdots).$$

Thus, substituting the expression for the f_l^k and transforming into the canonical basis, one finds

$$t_l^k + \sum_{ij} \bar{v}_{lj}^{ki} \rho_j^i = \varepsilon_k \delta_l^k,$$

where the one-body density is given by

$$\rho_j^i = \begin{cases} \delta_j^i, & \varepsilon_i \leq \varepsilon_F, \\ 0 & , \varepsilon_i > \varepsilon_F. \end{cases}$$

The HF equation

Finally, one obtains the HF equation:

$$\boxed{f_l^k = t_l^k + \sum_{\varepsilon_i \leq \varepsilon_F} \bar{v}_{li}^{ki} = \varepsilon_k \delta_l^k}$$

The HF equation

- Another way to derive the HF equation: The energy expectation value can be written as

$$E_0 = \langle \Phi | \hat{H} | \Phi \rangle = \sum_{\varepsilon_i \le \varepsilon_F} t_i^i + \frac{1}{2} \sum_{\varepsilon_i \le \varepsilon_F, \varepsilon_j \le \varepsilon_F} \bar{v}_{ij}^{ij}$$

$$= \sum_{\varepsilon_i \le \varepsilon_F} \langle \phi_i | (-\frac{\hbar^2}{2m} \nabla^2) | \phi_i \rangle + \frac{1}{2} \sum_{\varepsilon_i \le \varepsilon_F, \varepsilon_j \le \varepsilon_F} (\langle ij | V(\vec{r}_1, \vec{r}_2) | ij \rangle - \langle ij | V(\vec{r}_1, \vec{r}_2) | ji \rangle)$$

where the second term is

$$(\langle ij | V(\vec{r}_1, \vec{r}_2) | ij \rangle - \langle ij | V(\vec{r}_1, \vec{r}_2) | ji \rangle)$$

$$= \int d^3\vec{r}_1 \int d^3\vec{r}_2 \phi_i^*(\vec{r}_1) \phi_j^*(\vec{r}_2) v(\vec{r}_1, \vec{r}_2) \left[\phi_i(\vec{r}_1) \phi_j(\vec{r}_2) - \phi_j(\vec{r}_1) \phi_i(\vec{r}_2) \right]$$

The HF equation

The energy variation with respect to single-particle wave function $\phi_i^*(\vec{r}_1)$ (the factor 1/2 is removed considering the identical particles of 1 and 2)

$$\begin{aligned}
&\frac{\partial}{\partial\phi_i^*(\vec{r}_1)}\left[E_0-\varepsilon_i\int\phi_i^*(\vec{r}_1)\phi_i(\vec{r}_1)\right]\\
=\;&(-\frac{\hbar^2}{2m}\nabla^2)\phi_i(\vec{r}_2)+\int d^3\vec{r}_2\phi_j^*(\vec{r}_2)v(\vec{r}_1,\vec{r}_2)\phi_i(\vec{r}_1)\phi_j(\vec{r}_2)\\
&-\int d^3\vec{r}_2\phi_j^*(\vec{r}_2)v(\vec{r}_1,\vec{r}_2)\phi_j(\vec{r}_1)\phi_i(\vec{r}_2)-\varepsilon_i\phi_i(\vec{r}_1)\\
\equiv\;&(-\frac{\hbar^2}{2m}\nabla^2)\phi_i(\vec{r}_1)+V_H(\vec{r}_1)\phi_i(\vec{r}_1)-\int d^3\vec{r}_2\,V_F(\vec{r}_1,\vec{r}_2)\phi_i(\vec{r}_2)-\varepsilon_i\phi_i(\vec{r}_1),\qquad(6)
\end{aligned}$$

where

$$V_H(\vec{r}_1)=\sum_{\varepsilon_j\le\varepsilon_F}\int d^3\vec{r}_2\phi_j^*(\vec{r}_2)v(\vec{r}_1,\vec{r}_2)\phi_j(\vec{r}_2),$$

$$V_F(\vec{r}_1,\vec{r}_2)=\sum_{\varepsilon_j\le\varepsilon_F}\phi_j^*(\vec{r}_2)v(\vec{r}_1,\vec{r}_2)\phi_j(\vec{r}_1).$$

Thus, the variational principle leads to the HF equation in coordinate space

$$\boxed{-\frac{\hbar^2}{2m}\nabla^2\phi_i(\vec{r}_1)+V_H(\vec{r}_1)\phi_i(\vec{r}_1)-\int d^3\vec{r}_2\,V_F(\vec{r}_1,\vec{r}_2)\phi_i(\vec{r}_2)=\varepsilon_i\phi_i(\vec{r}_1).}$$

The density matrix

The density matrix

Given a many-particle state $|\Phi\rangle$, the one-particle density matrix is defined as

$$\rho_k^l = \rho_{kl} \equiv \left\langle \Phi \left| \hat{a}_l^\dagger \hat{a}_k \right| \Phi \right\rangle$$

where k and l run over the one-particle basis states.

- $|\Phi\rangle$ need not be a simple Slater determinant built out of these states but can be a general superposition of such Slater determinants.
- The one-particle density matrix depends on both the state $|\Phi\rangle$ and the single-particle basis defined by $a_k^\dagger, a_l$.
- ρ_{kl} is hermitian: $\rho_{kl} = \rho_{lk}^*$

If $|\Phi\rangle$ is a simple Slater determinant, the density matrix element

$$\rho_j^i = \begin{cases} \delta_j^i, & \varepsilon_i \leq \varepsilon_F, \\ 0 & , \varepsilon_i > \varepsilon_F. \end{cases}$$

The excited states

The excited states

- excitation configurations:
  The one-particle one-hole excitation configuration on top of the HF state,

$$|\Phi_i^m\rangle \equiv |m,i\rangle = a_m^\dagger a_i |\Phi\rangle$$

  The two-particle two-hole excitation configuration on top of the HF state,

$$|\Phi_{ij}^{mn}\rangle \equiv |mn,ij\rangle = a_m^\dagger a_n^\dagger a_i a_j |\Phi\rangle$$

- Energies of excitation configurations:
  The energy of the one-particle one-hole excitation configuration

$$E_i^m \equiv \langle mi|H|mi\rangle = \langle \Phi|a_i^\dagger a_m H a_m^\dagger a_i|\Phi\rangle = E_0 + \varepsilon_m - \varepsilon_i - \bar{v}_{mimi}.$$

  Homework: prove the above relation.

The excited states

The energy of one-particle removed configuration is given by

$$E_j = \langle \Phi | a_j^\dagger H a_j | \Phi \rangle = \sum_{i \neq j} t_{ii} + \frac{1}{2} \sum_{i_1, i_2 \neq j} \bar{v}_{i_1 i_2 i_1 i_2}$$

and the difference from the ground-state energy becomes

$$\begin{aligned} E_j - E_{\mathrm{HF}} &= -t_{jj} - \frac{1}{2} \sum_i \bar{v}_{ijij} - \frac{1}{2} \sum_i \bar{v}_{jiji} \\ &= -t_{jj} - \sum_i \bar{v}_{ijij} \\ &= -\varepsilon_j \end{aligned}$$

Here the symmetry of the matrix elements $\bar{v}_{ijj} = \bar{v}_{jiji}$ was used. Thus the single-particle energy ε_j indicates the energy required to remove a particle from the nucleus. This is the contents of Koopman's theorem.

The HF approach with Skyrme forces

The Skyrme HF

Milestone

Access by Sun Yat-Sen University Go Mobile »

Hartree-Fock Calculations with Skyrme's Interaction. I. Spherical Nuclei

D. Vautherin and D. M. Brink
Phys. Rev. C **5**, 626 – Published 1 March 1972

An article within the collection: *Physical Review C* 50th Anniversary Milestones

Article References Citing Articles (1,457) PDF Export Citation

ABSTRACT

Hartree-Fock calculations for spherical nuclei using Skyrme's density-dependent effective nucleon-nucleon interaction are discussed systematically. Skyrme's interaction is described and the general formula for the mean energy of a spherical nucleus derived. Hartree-Fock equations are obtained by varying the mean energy with respect to the single-particle wave functions of occupied states. Relations between the parameters of the Skyrme force and various general properties of nuclear matter and finite nuclei are analyzed. Calculations have been made for closed-shell nuclei using two rather different sets of parameters, both of which give good binding energies and radii for ^{16}O and ^{208}Pb. Both interactions give good binding energies and charge radii for all closed-shell nuclei. Calculated electron scattering angular distributions agree qualitatively with experiment, and for one interaction there is good quantitative agreement. The single-particle energies calculated with the two interactions are somewhat different owing to a different nonlocality of the Hartree-Fock potentials, but both interactions give the correct order and density of single-particle levels near the Fermi level. They differ most strongly in their predictions for the energies of $1s$ single-particle states.

Received 15 November 1971

DOI: https://doi.org/10.1103/PhysRevC.5.626

Issue

Vol. 5, Iss. 3 — March 1972

Reuse & Permissions

The Skyrme HF

The Skyrme interaction is a sum of two- and three-body parts,

$$\hat{H} = \sum_i \hat{t}_i + \sum_{i<j} v_{ij}^{(2)} + \sum_{i<j<k} v_{ijk}^{(3)}$$

the two body part was given by

$$\begin{aligned} v_{12}^{(2)} =& t_0 \left(1 + x_0 \hat{P}_\sigma\right) \delta\left(r_1 - r_2\right) \\ &+ \frac{1}{2} t_1 \left(\delta\left(\boldsymbol{r}_1 - \boldsymbol{r}_2\right) \hat{k}^2 + \hat{k}'^2 \delta\left(\boldsymbol{r}_1 - \boldsymbol{r}_2\right)\right) \\ &+ t_2 \hat{\boldsymbol{k}} \cdot \delta\left(\boldsymbol{r}_1 - \boldsymbol{r}_2\right) \hat{\boldsymbol{k}}' + \mathrm{i} W_0 \left(\hat{\boldsymbol{\sigma}}_1 + \hat{\boldsymbol{\sigma}}_2\right) \cdot \hat{\boldsymbol{k}}' \times \delta\left(\boldsymbol{r}_1 - \boldsymbol{r}_2\right) \hat{\boldsymbol{k}} \end{aligned}$$

and the three-body part by

$$v_{123}^{(3)} = t_3 \delta\left(\boldsymbol{r}_1 - \boldsymbol{r}_2\right) \delta\left(\boldsymbol{r}_2 - \boldsymbol{r}_3\right)$$

D. Vautherin and D. M. Brink, Phys. Rev. C 5, 626 (1972)

The Skyrme HF

The operators $\hat{\boldsymbol{k}}$ and $\hat{\boldsymbol{k}}'$ are defined as

$$\hat{\boldsymbol{k}} = \frac{1}{2\mathrm{i}}\left(\overrightarrow{\nabla}_1 - \overrightarrow{\nabla}_2\right) \quad , \quad \hat{\boldsymbol{k}}' = -\frac{1}{2\mathrm{i}}\left(\overleftarrow{\nabla}_1 - \overleftarrow{\nabla}_2\right)$$

and that $\hat{\boldsymbol{k}}'$ acts to the left.
The expectation value of the Hamiltonian in a Slater determinant $|\mathrm{HF}\rangle$ is given by

$$\begin{aligned} E &= \langle \mathrm{HF}|\hat{H}|\mathrm{HF}\rangle \\ &= \sum_i \langle i|\hat{t}|i\rangle + \frac{1}{2}\sum_{ij}\left\langle ij\left|\bar{v}^{(2)}\right|ij\right\rangle + \frac{1}{6}\sum_{ijk}\left\langle ijk\left|\bar{v}^{(3)}\right|ijk\right\rangle \end{aligned}$$

The energy can be rewritten as a spatial integral over a Hamiltonian density,

$$E = \int \mathrm{d}^3 r \hat{\mathcal{H}}(\boldsymbol{r}).$$

D. Vautherin and D. M. Brink, Phys. Rev. C 5, 626 (1972)

The Skyrme HF

家庭作业选做题：在HF近似下，推导Skyrme核力对应的能量密度表达式$\hat{\mathcal{H}}(\boldsymbol{r})$:

$$\begin{aligned}\hat{\mathcal{H}}(\boldsymbol{r}) =& \frac{\hbar^2}{2m}\tau(\mathbf{r}) + \frac{1}{2}t_0\left[\left(1+\frac{1}{2}x_0\right)\rho^2 - \left(x_0+\frac{1}{2}\right)\left(\rho_n{}^2+\rho_p^2\right)\right] \\ &+ \frac{1}{4}\left(t_1+t_2\right)\rho\tau + \frac{1}{8}\left(t_2-t_1\right)\left(\rho_n\tau_n+\rho_p\tau_p\right) + \frac{1}{16}\left(t_2-3t_1\right)\rho\nabla^2\rho \\ &+ \frac{1}{32}\left(3t_1+t_2\right)\left(\rho_n\nabla^2\rho_n+\rho_p\nabla^2\rho_p\right) + \frac{1}{16}\left(t_1-t_2\right)\left(\vec{J}_n^2+\vec{J}_p^2\right) \\ &+ \frac{1}{4}t_3\rho_n\rho_p\rho + \hat{\mathcal{H}}_C(\mathbf{r}) - \frac{1}{2}W_0\left(\rho\vec{\nabla}\cdot\vec{J}+\rho_n\vec{\nabla}\cdot\vec{J}_n+\rho_p\vec{\nabla}\cdot\vec{J}_p\right)\end{aligned}$$

where the Coulomb energy

$$\hat{\mathcal{H}}_C(\mathbf{r}) = \frac{1}{2}\rho(\mathbf{r})\int d\mathbf{r}'\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}\rho(\mathbf{r}')d\mathbf{r}'$$

and densities are defined as ($q = n, p$, and $\rho = \rho_n + \rho_p$)

$$\begin{aligned}\rho_q(\mathbf{r}) &= \textstyle\sum_{i,\sigma}|\phi_i(\mathbf{r},\sigma,q)|^2 \\ \tau_a(\mathbf{r}) &= \textstyle\sum_{i,\sigma}\left|\vec{\nabla}\phi_i(\mathbf{r},\sigma,q)\right|^2, \\ \vec{J}_q(\mathbf{r}) &= (-i)\textstyle\sum_{i,\sigma,\sigma'}\phi_i^*(\mathbf{r},\sigma,q)\left[\vec{\nabla}\phi_i\left(\mathbf{r},\sigma',q\right)\times\langle\sigma|\vec{\sigma}|\sigma'\rangle\right]\end{aligned}$$

D. Vautherin and D. M. Brink, Phys. Rev. C 5, 626 (1972)

The Skyrme HF

$$\left[-\vec{\nabla}\cdot\frac{\hbar^2}{2m_q^*(\vec{r})}\vec{\nabla}+U_q(\vec{r})+\vec{W}_q(\vec{r})\cdot(-i)(\vec{\nabla}\times\vec{\sigma})\right]\phi_i=e_i\phi_i\,, \tag{20}$$

where q stands for the charge of the single-particle state i. Equation (20) has the form of a local Schrödinger equation with an effective mass $m^*(\vec{r})$ which depends on the density only,

$$\frac{\hbar^2}{2m_q^*(\vec{r})}=\frac{\hbar^2}{2m}+\tfrac{1}{4}(t_1+t_2)\rho+\tfrac{1}{8}(t_2-t_1)\rho_q\,; \tag{21}$$

whereas, the potential $U(\vec{r})$ also depends on the kinetic energy density,

$$\begin{aligned}U_q(\vec{r})=t_0\big[(1+\tfrac{1}{2}x_0)\rho-(x_0+\tfrac{1}{2})\rho_q\big]+\tfrac{1}{4}t_3(\rho^2-\rho_q{}^2)\\ -\tfrac{1}{8}(3t_1-t_2)\nabla^2\rho+\tfrac{1}{16}(3t_1+t_2)\nabla^2\rho_q+\tfrac{1}{4}(t_1+t_2)\tau\\ +\tfrac{1}{8}(t_2-t_1)\tau_q-\tfrac{1}{2}W_0(\vec{\nabla}\cdot\vec{J}+\vec{\nabla}\cdot\vec{J}_q)+\delta_{q,+\frac{1}{2}}V_C(\vec{r})\,.\end{aligned} \tag{22a}$$

The form factor $\vec{W}$ of the one-body spin-orbit potential is

$$\vec{W}_q(\vec{r})=\tfrac{1}{2}W_0(\vec{\nabla}\rho+\vec{\nabla}\rho_q)+\tfrac{1}{8}(t_1-t_2)\vec{J}_q(\vec{r})\,. \tag{22b}$$

In expression (22a) V_C is the direct part of the Coulomb potential defined by equation (13). The Coulomb exchange term has been neglected. One

For doubly-closed-shell nuclei the reduction of angular variables in the Hartree-Fock equations can be carried out by making the ansatz

$$\phi_i(\vec{r},\sigma,\tau)=\frac{R_\alpha(r)}{r}\mathcal{Y}_{ljm}(\hat{r},\sigma)\chi_q(\tau)\,, \tag{26}$$

where

$$\mathcal{Y}_{ljm}(\hat{r},\sigma)=\sum_{m_l m_s}\langle l\tfrac{1}{2}m_l m_s|jm\rangle\, Y_{lm_l}(\hat{r})\chi_{m_s}(\sigma)\,,$$

and where the index i now stands for the following set of quantum numbers: the charge q, the principal quantum number n, the orbital angular momentum l, the total angular momentum j, and the magnetic quantum number m. We have also introduced the notation $\alpha\equiv q,n,l,j$ for simplicity.

From the definitions (11) for the density $\rho(\vec{r})$ and the kinetic energy density $\tau(\vec{r})$ one concludes that these functions depend on the radial coordinate r only. Explicitly,

$$\begin{aligned}\rho(r)&=\frac{1}{4\pi r^2}\sum_\alpha(2j_\alpha+1)R_\alpha{}^2(r)\,,\\ \tau(r)&=\frac{1}{4\pi}\sum_\alpha(2j_\alpha+1)\left[\left(\frac{d\varphi_\alpha}{dr}\right)^2+\frac{l_\alpha(l_\alpha+1)}{r^2}\varphi_\alpha{}^2\right],\end{aligned} \tag{27}$$

The Skyrme HF

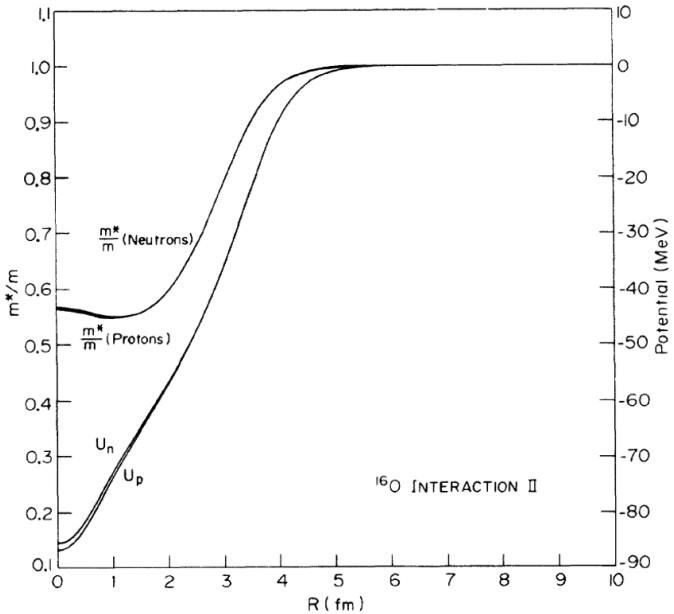


FIG. 10. Effective mass m^*/m and potential U calculated in ^{16}O with interaction II.

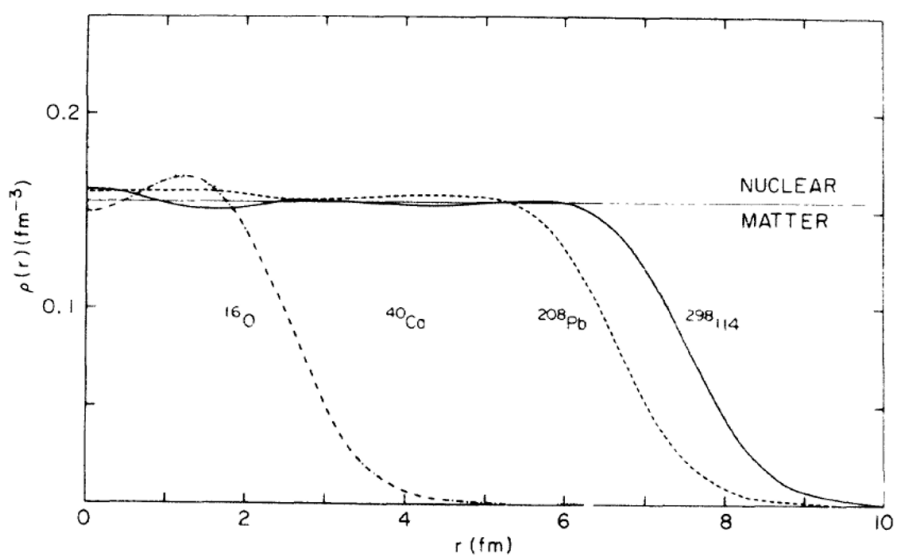
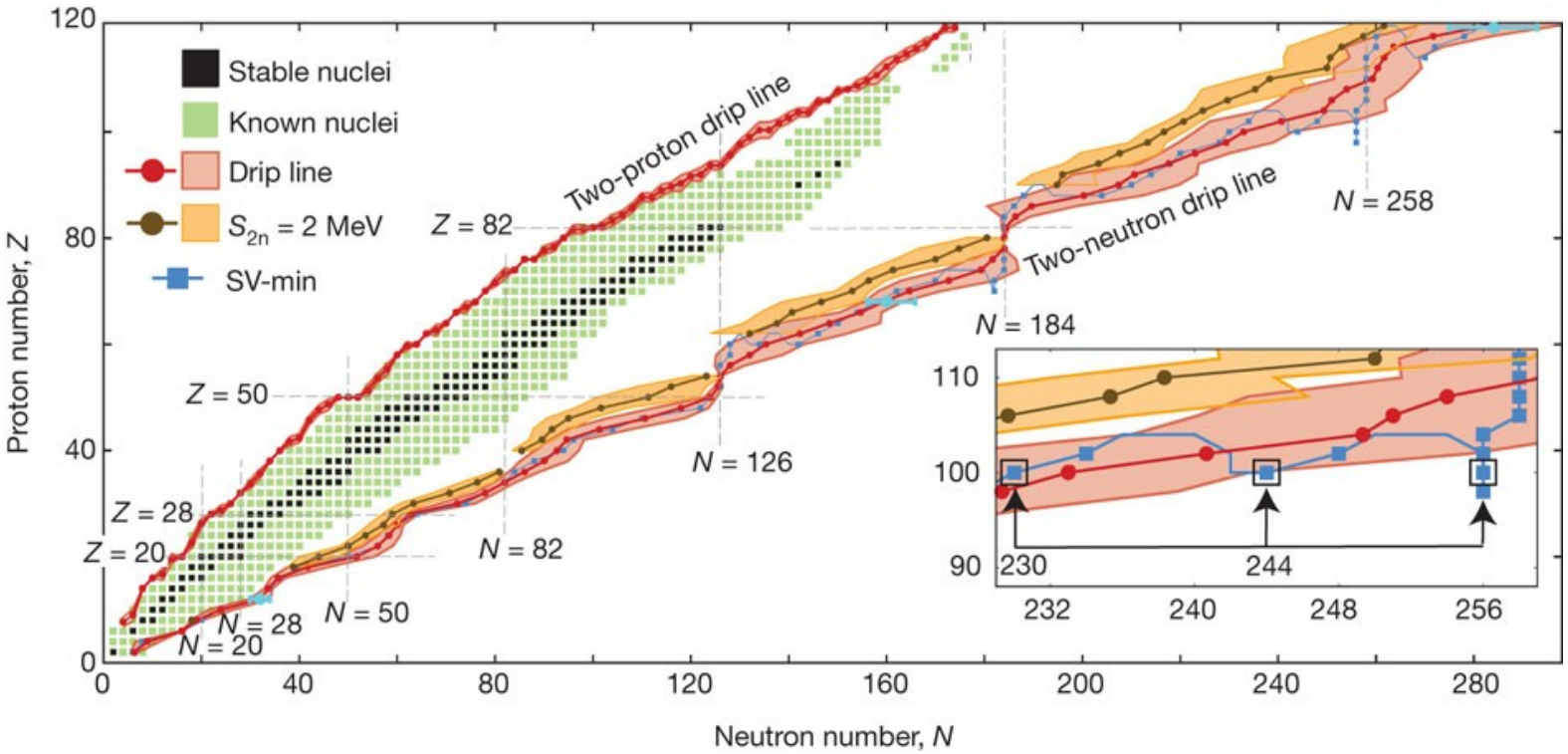


FIG. 1. Mass distributions $\rho(r)$ calculated with interaction I for the nuclei ^{16}O, ^{40}Ca, ^{208}Pb, and ^{298}114.

D. Vautherin and D. M. Brink, Phys. Rev. C 5, 626 (1972)

The limits of the nuclear landscape by Skyrme DFT approach



- Several Skyrme interactions were used
- The number of bound nuclides with between 2 and 120 protons is around 7,000.

J. Erler et al., Nature 486, 509–512 (2012)

The Skyrme HF for nuclear masses

Different DFT mass tables are compiled and can be downloaded here:
http://massexplorer.frib.msu.edu/content/DFTMassTables.html