Double Exchange *IV*: *Ligand Field Effects*

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Ligand-Field Theory

Part I: A Simple Introduction(07/31/2020)

Part II: Molecular-orbital theory (Covalent Bond Theory)

II.I: Magnetic State for Insulators

II.II: $3d^1$ Covalent Bond Method(2 Month)

II.III: Superexchange

II.IV: Goodenough-Kanamori Rule (3 Months)

Part III: Crystal Field theory (Electrostatic Theory)

III.I: $3d^1$ Model-Based Method (07/03/2020)

III.II: $3d^1$ Symmetry-Based Method (1 Months)

III.III: $3d^N, \mathrm{N} \geq 2$ Model-Based Method (4 Months)

III.IV: $3d^1$ Model-Based Method: Phillips-Cohen-Heine Theorem (5 Months)

Part II.I: Magnetic State for Insulators

P.W. Anderson, Ch.2: Exchange in Insulators: Superexchange, Direct Exchange, and Double Exchange; Magnetism Volume I Edited by G. T. Rado & H. Suhl

Bohr–van Leeuwen Theorem: Non-existence of Classical Magnetism

Assumptions

(1) $$\mathcal{H}(\{\vec{r}_j\},\{\vec{p}_j\};B) := \sum_{j=1}^{N}\left[\frac{1}{2m}\left(\vec{p}_j+\frac{e}{c}\vec{A}(\vec{r}_j)\right)^2 + U_{el}(\vec{r}_j)+U_c(\vec{r}_j)\right] + U_{int}(\vec{r}_1,\vec{r}_2,\dots,\vec{r}_N)$$

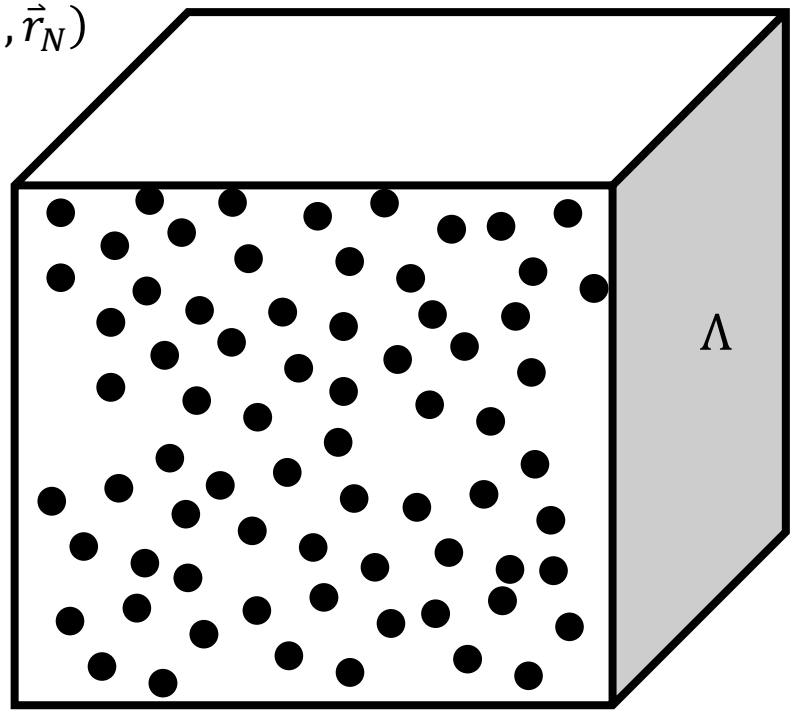
$\vec{A}(\vec{r}_j)$: vector potential; $U_{el}(\vec{r}_j)$: electric potential energy ;

$U_c(\vec{r}_j)$: confinement potential; U_{int}: many-body interactions

(2) No mass center rotation, only translational degree of freedom

(3) In thermal equilibrium with a heat bath (Canonical Ensemble)

Finite System as an Example



N Classical Electrons

Peierls R.H., Surprises in Theoretical Physics (Princeton University Press, Princeton) 1972.

Baptiste Savoie. A rigorous proof of the Bohr-van Leeuwen theorem in the semiclassical limit.. 2014.hal-00958203v3.

Van Vleck J. H., The Theory of Electric and Magnetic Susceptibilities (Oxford University Press, London) 1932;

Bohr–van Leeuwen Theorem: Non-existence of Classical Magnetism

$$\mathcal{F}(\beta, N, V(\Lambda); B) := \frac{\langle E \rangle - TS}{V(\Lambda)} = -\frac{1}{V(\Lambda)\beta} \ln(\mathcal{Z}(\beta, N, V(\Lambda); B))$$

Wikipedia: Partition Function

$$\mathcal{Z}(\beta, N, V(\Lambda); B) = \frac{1}{h^{3N} N!} \int d\vec{r}_1 \dots d\vec{r}_N d\vec{p}_1 \dots d\vec{p}_N e^{-\beta \mathcal{H}(\{\vec{r}_j\}, \{\vec{p}_j\}; B)}$$

h^{3N} added to solve the **entropy paradox of classical thermodynamics**

$$\mathcal{M}(\beta, N, V(\Lambda); B) := -\frac{\partial \mathcal{F}}{\partial B} = \frac{1}{V(\Lambda)\beta} \frac{\partial ln(\mathcal{Z}(\beta, N, V(\Lambda); B))}{\partial B}$$

Canonical Transformation:

$$\{\vec{p}_j, \vec{r}_j\} \to \left\{\vec{p}_j^{\,0} = \vec{p}_j + \frac{e}{c}\vec{A}(\vec{r}_j), \vec{r}_j\right\} \qquad J = \left|\frac{\partial(\vec{p}_j, \vec{r}_j)}{\partial(\vec{p}_j^{\,0}, \vec{r}_j)}\right| = 1$$

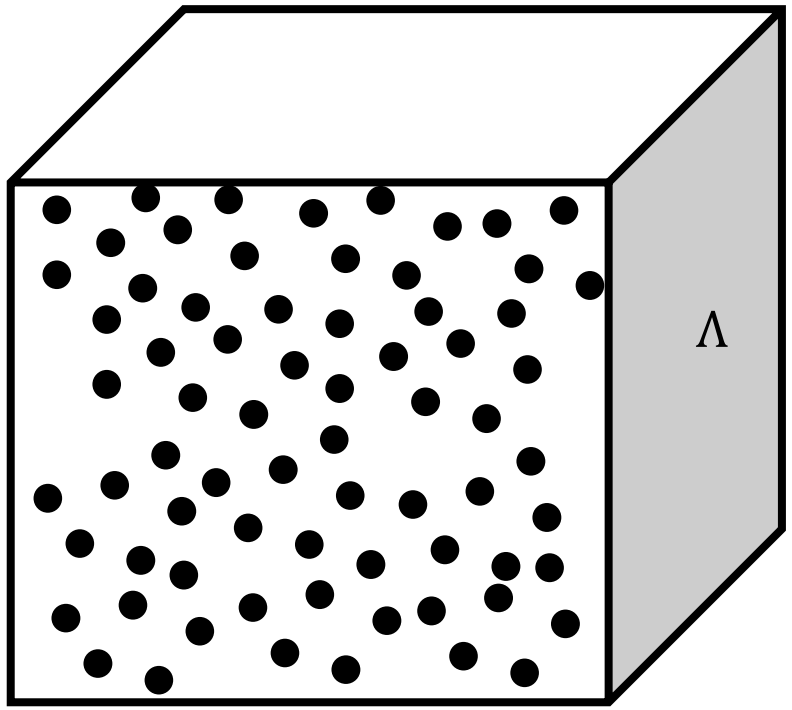
$$\mathcal{H}(\{\vec{r}_j\}, \{\vec{p}_j\}; B) \qquad d\vec{r}_1 \dots d\vec{r}_N d\vec{p}_1 \dots d\vec{p}_N$$

$$\mathcal{H}'(\{\vec{r}_j\}, \{\vec{p}_j^{\,0}\}; B) = \mathcal{H}(\{\vec{r}_j\}, \{\vec{p}_j\}; B = 0) \qquad d\vec{r}_1 \dots d\vec{r}_N d\vec{p}_1^{\,0} \dots d\vec{p}_N^{\,0}$$

$$\mathcal{Z}(\beta, N, V(\Lambda); B) = \frac{1}{h^{3N} N!} J \int d\vec{r}_1 \dots d\vec{r}_N d\vec{p}_1^{\,0} \dots d\vec{p}_N^{\,0} e^{-\beta \mathcal{H}(\{\vec{r}_j\}, \{\vec{p}_j\}; B=0)} = \mathcal{Z}(\beta, N, V(\Lambda); B = 0)$$

$$\mathcal{M}(\beta, N, V(\Lambda); B) = 0 \quad !!!$$

Finite System as an Example



***N* Classical Electrons**

$$\mathcal{H}(\{\vec{r}_j\}, \{\vec{p}_j\}; B) := \sum_{j=1}^{N} \left[\frac{1}{2m}\left(\vec{p}_j + \frac{e}{c}\vec{A}(\vec{r}_j)\right)^2 + U_{el}(\vec{r}_j) + U_c(\vec{r}_j)\right] + U_{int}(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$$

Heisenberg-Dirac Exchange Interaction

Assumptions

(1) **N orthonormal Orbits** $|\alpha_1\rangle, |\alpha_2\rangle, \dots, |\alpha_N\rangle$; $|\alpha\rangle \equiv |\alpha_1, \alpha_2, \dots, \alpha_N\rangle$ $\quad |\vec{r}\rangle \equiv |\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N\rangle \quad |\sigma\rangle \equiv |\sigma_1, \sigma_2, \dots, \sigma_N\rangle$

$P^\alpha|\alpha\rangle \equiv |\alpha_i, \alpha_j, \dots, \alpha_k\rangle \qquad P^\sigma|\sigma\rangle \equiv |\sigma_m, \sigma_n, \dots, \sigma_t\rangle \qquad \boldsymbol{P} \in \mathbb{P}$ ={N! permutations of 1,2,3…N}

$H_0|\Psi\rangle = E_0|\Psi\rangle \qquad |\Psi\rangle = |\psi\rangle|\chi\rangle$ Spin-Statistics Theorem $\quad P_{ij}|\Psi\rangle = (P^\alpha{}_{ij}|\psi\rangle)(P^\sigma{}_{ij}|\chi\rangle) = -|\psi\rangle|\chi\rangle = -|\Psi\rangle$

$$|\psi\rangle \equiv \frac{1}{\sqrt{N!}}\sum_{P^\alpha\in\mathbb{P}} P^\alpha|\alpha\rangle \quad |\chi\rangle \equiv \frac{1}{\sqrt{N!}}\sum_{P^\sigma\in\mathbb{P}} (-1)^{S_{P^\sigma}} P^\sigma|\sigma\rangle \qquad |\psi\rangle \equiv \frac{1}{\sqrt{2}}[|\alpha_1,\alpha_2\rangle + |\alpha_2,\alpha_1\rangle] \qquad |\chi\rangle \equiv \frac{1}{\sqrt{2}}[|1,-1\rangle - |-1,1\rangle]$$

(2) Perturbation Problem: $\langle\Psi|V|\Psi\rangle = \langle\psi|V|\psi\rangle \ll \langle\psi|H_0|\psi\rangle$

(3) $\langle P\vec{r}|V|P\vec{r}'\rangle = \langle\vec{r}|V|\vec{r}'\rangle \qquad \boldsymbol{V} = \frac{1}{2}\sum_{i,j}^{N_e}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} \qquad \int d\vec{r}|\vec{r}\rangle\langle\vec{r}| = \int d\vec{r}|P\vec{r}\rangle\langle P\vec{r}| = 1$

$\langle\vec{r}'|P_b\alpha\rangle = \langle P\vec{r}'|P_bP\alpha\rangle \qquad \langle P_a\alpha|\vec{r}\rangle = \langle P_aP\alpha|P\vec{r}\rangle$

$$\langle P^\alpha{}_a\alpha|V|P^\alpha{}_b\alpha\rangle$$

$$= \int d\vec{r}d\vec{r}'\langle P^\alpha{}_a\alpha|\vec{r}\rangle\langle\vec{r}|V|\vec{r}'\rangle\langle\vec{r}'|P^\alpha{}_b\alpha\rangle = \int d\vec{r}d\vec{r}'\langle P^\alpha{}_aP\alpha|P\vec{r}\rangle\langle\vec{r}|V|\vec{r}'\rangle\langle P\vec{r}'|P^\alpha{}_bP\alpha\rangle$$

$$= \int d\vec{r}d\vec{r}'\langle P^\alpha{}_aP\alpha|P\vec{r}\rangle\langle P\vec{r}|V|P\vec{r}'\rangle\langle P\vec{r}'|P^\alpha{}_bP\alpha\rangle = \int d\vec{r}d\vec{r}'\langle P^\alpha{}_aP\alpha|\vec{r}\rangle\langle\vec{r}|V|\vec{r}'\rangle\langle\vec{r}'|P^\alpha{}_bP\alpha\rangle = \langle P^\alpha{}_aP\alpha|V|P^\alpha{}_bP\alpha\rangle$$

P.A.M.Dirac, Proc.Roy.Soc. A123, 714 (1929)

Heisenberg-Dirac Exchange Interaction

$P_a P_b{}^{-1} \in \mathbb{P}$ ={N! permutations of 1,2,3…N}

$$\boldsymbol{P} = \boldsymbol{P^{\alpha}{}_b}^{-1}$$

$$\langle \boldsymbol{P^{\alpha}{}_a \alpha} | \boldsymbol{V} | \boldsymbol{P^{\alpha}{}_b \alpha} \rangle = \langle \boldsymbol{P^{\alpha}{}_a P \alpha} | \boldsymbol{V} | \boldsymbol{P^{\alpha}{}_b P \alpha} \rangle = \left\langle P^{\alpha}{}_a P^{\alpha}{}_b{}^{-1} \alpha \middle| V \middle| \alpha \right\rangle \equiv V_{P'^{\alpha}}$$

$$P'^{\alpha} \equiv P^{\alpha}{}_a P^{\alpha}{}_b{}^{-1}$$

$\boldsymbol{n}! \times \boldsymbol{n}!$ $\qquad$ $\boldsymbol{n}!$

$$\sum_{P^{\alpha}} |P^{\alpha}\alpha\rangle\langle P^{\alpha}\alpha| = 1$$

$$l.h.s = \sum_{P_a} \langle \vec{r} | \boldsymbol{P^{\alpha}{}_a \alpha} \rangle \langle \boldsymbol{P^{\alpha}{}_a} \alpha | V | \boldsymbol{P^{\alpha}{}_b} \alpha \rangle = \langle \vec{r} | V | \boldsymbol{P^{\alpha}{}_b} \alpha \rangle = r.h.s = \sum_{P_a} \langle \vec{r} | \boldsymbol{P^{\alpha}{}_a \alpha} \rangle V_{P'} = \sum_{P'^{\alpha}} \langle \vec{r} | P'^{\alpha} \boldsymbol{P^{\alpha}{}_b \alpha} \rangle V_{P'} = \langle \vec{r} | \textstyle\sum_{\boldsymbol{P'^{\alpha}}} \boldsymbol{V_{P'^{\alpha}} P'^{\alpha}} | \boldsymbol{P^{\alpha}{}_b \alpha}$$

$$\Longrightarrow \boldsymbol{V} = \sum_{\boldsymbol{P'^{\alpha}}} \boldsymbol{V_{P'^{\alpha}} P'^{\alpha}} \quad \text{If } \boldsymbol{V} = \frac{1}{2} \sum_{i,j}^{N_e} \frac{e^2}{|\boldsymbol{r_i} - \boldsymbol{r_j}|} \Longrightarrow \boldsymbol{V} = \boldsymbol{V_I} + \sum_{\boldsymbol{i<j}} \boldsymbol{V_{ij} P^{\alpha}{}_{ij}}$$

$\forall \left| \boldsymbol{\Psi_n} \right\rangle$

$$\boldsymbol{P^{\alpha}{}_{ij}} |\Psi_n\rangle = (\boldsymbol{P^{\alpha}{}_{ij}} |\psi_{\boldsymbol{n}}\rangle) |\chi_n\rangle = -|\psi_{\boldsymbol{n}}\rangle (\boldsymbol{P_{ij}}^{\sigma} |\chi_n\rangle) = -\boldsymbol{P_{ij}}^{\sigma} |\Psi_n\rangle \Longrightarrow \boldsymbol{P^{\alpha}{}_{ij}} = -\boldsymbol{P_{ij}}^{\sigma}$$

$$\boldsymbol{P_{ij}}^{\sigma} = \frac{1}{2}\{1 + \vec{\sigma}_i \cdot \vec{\sigma}_j\} \in \{1, \vec{\sigma}_i\} \otimes \{1, \vec{\sigma}_j\} \qquad \left\{ \left| s_i = \frac{1}{2}, s_{iz} = \pm\frac{1}{2} \right\rangle \right\} \otimes \left\{ \left| s_j = \frac{1}{2}, s_{jz} = \pm\frac{1}{2} \right\rangle \right\} \qquad \vec{s}_i = \frac{1}{2}\vec{\sigma}_i$$

$$V = V_I - \sum_{i<j} V_{ij} \frac{1}{2}\{1 + \vec{\sigma}_i \cdot \vec{\sigma}_j\} = V_I - \sum_{i<j} J_{ij} \left\{ \frac{1}{4} + \vec{s}_i \cdot \vec{s}_j \right\}$$

$$\boldsymbol{P_{ij}}^{\sigma} \vec{\sigma}_i \boldsymbol{P_{ij}}^{\sigma^{-1}} = \vec{\sigma}_j$$

$$V_I \equiv \langle \alpha | V | \alpha \rangle \qquad J_{ij} \equiv \left\langle \alpha_j \alpha_i \middle| \frac{e^2}{|\boldsymbol{r_i} - \boldsymbol{r_j}|} \middle| \alpha_i \alpha_j \right\rangle$$

$$\boldsymbol{P_{ij}}^{\sigma} \vec{\sigma}_j \boldsymbol{P_{ij}}^{\sigma^{-1}} = \vec{\sigma}_i$$

P.A.M.Dirac, Proc.Roy.Soc. A123, 714 (1929)

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Method to Calculate Ground State and Energy

Energy Functional $\varepsilon[\Psi] = \dfrac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$

1) $\varepsilon \geq E_0, E_0$ the ground state of Hamiltonian $\hat{H}$

2) $\varepsilon = E_0$, iff Ψ is the ground state

Proof: **Spectral Theorem:** $\hat{H} = \int dE|E\rangle E\langle E|$ $\quad \hat{I} = \int dE|E\rangle\langle E|$ $\quad \hat{H}|E\rangle = E|E\rangle \quad E \geq E_0$

$$\varepsilon[\Psi] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\int dE E|\langle\Psi|E\rangle|^2}{\langle\Psi|\Psi\rangle} \geq \frac{\int dE E_0|\langle\Psi|E\rangle|^2}{\langle\Psi|\Psi\rangle} = \frac{E_0\int dE|\langle\Psi|E\rangle|^2}{\langle\Psi|\Psi\rangle}$$

$$= \frac{E_0\langle\Psi|\hat{I}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = E_0; \quad \text{iff } |\Psi\rangle = |E_0\rangle, \varepsilon[\Psi] = E_0$$

$$\frac{\delta\varepsilon[\Psi]}{\delta\Psi} = 0, \frac{\delta^2\varepsilon[\Psi]}{\delta\Psi^2} > 0 \quad \Rightarrow \quad |\Psi\rangle \approx |E_0\rangle$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Hartree-Fock Equation

$$T_e(\boldsymbol{r}) \equiv \sum_{i=1}^{N_e} \frac{\boldsymbol{p}_i^2}{2m_i} \qquad V_{eN}(\boldsymbol{r},\boldsymbol{R}) \equiv -\sum_{I,i}^{N,N_e} \frac{Z_I e^2}{|\boldsymbol{R}_I - \boldsymbol{r}_i|}$$

With respect to the changes in the orbitals $\boldsymbol{\psi}_i \to \boldsymbol{\psi}_i + \boldsymbol{\delta\psi}_i$

$$V_{ee}(\boldsymbol{r}) \equiv \frac{1}{2}\sum_{i,j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} = \sum_{i>j}^{N_e} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

Minimize $\quad E_{HF}[\Psi] = \langle \Psi | \hat{H}_e | \Psi \rangle = E_e[\{\boldsymbol{\psi}_i\}]$

$$\boldsymbol{H}_e(\boldsymbol{r},\boldsymbol{R}) \equiv [\boldsymbol{T}_e(\boldsymbol{r}) + \boldsymbol{V}_{eN}(\boldsymbol{r},\boldsymbol{R})] + \boldsymbol{V}_{ee}(\boldsymbol{r}) = \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij} \qquad h_i \equiv \frac{\boldsymbol{p}_i^2}{2m_i} - \sum_{I}^{N} \frac{Z_I e^2}{|\boldsymbol{R}_I - \boldsymbol{r}_i|} \qquad v_{ij} \equiv \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|}$$

Lagrange Multipliers Method

$$\mathcal{L}[\{\boldsymbol{\psi}_i\}] \equiv E_e[\{\boldsymbol{\psi}_i\}] - \boxed{\sum_{i,j} \epsilon_{ij} \left(\langle \boldsymbol{\psi}_i | \boldsymbol{\psi}_j \rangle - \delta_{ij} \right)}$$

Keep ψ_i orthonormal

$$\frac{\delta \mathcal{L}[\{\boldsymbol{\psi}_i\}]}{\delta \boldsymbol{\psi}_i^{\dagger}} = 0 \quad \Rightarrow$$

Hartree-Fock Equation

"Self-consistent Field Theory"

$$h_i \psi_i(\boldsymbol{r}_i,\boldsymbol{\sigma}_i) + \left[\sum_j^{N_e} \int d\boldsymbol{r}_j \, v_{ij} |\psi_j(\boldsymbol{r}_j,\boldsymbol{\sigma}_j)|^2 \right] \psi_i(\boldsymbol{r}_i,\boldsymbol{\sigma}_i) - \sum_j^{N_e} \int d\boldsymbol{r}_j \, \psi_j^{\dagger}(\boldsymbol{r}_j,\boldsymbol{\sigma}_j) \psi_i(\boldsymbol{r}_j,\boldsymbol{\sigma}_j) v_{ij} \psi_j(\boldsymbol{r}_i,\boldsymbol{\sigma}_i) = \epsilon_i \psi_i(\boldsymbol{r}_i,\boldsymbol{\sigma}_i)$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Initialize Wavefunction

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle$$

Spin-Statistics Theorem

$$\Psi(r,\sigma) = \frac{1}{\sqrt{N_e!}} \begin{vmatrix} \psi_1(r_1) & \psi_2(r_1) & \cdots & \psi_{N_e}(r_1) \\ \psi_1(r_2) & \psi_2(r_2) & \cdots & \psi_{N_e}(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_{N_e}) & \psi_2(r_{N_e}) & \cdots & \psi_{N_e}(r_{N_e}) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N_e!}} \epsilon_{i_1 i_2 \ldots i_{N_e}} \psi_{i_1}(r_1) \psi_{i_2}(r_2) \ldots \psi_{i_{N_e}}(r_{N_e})$$

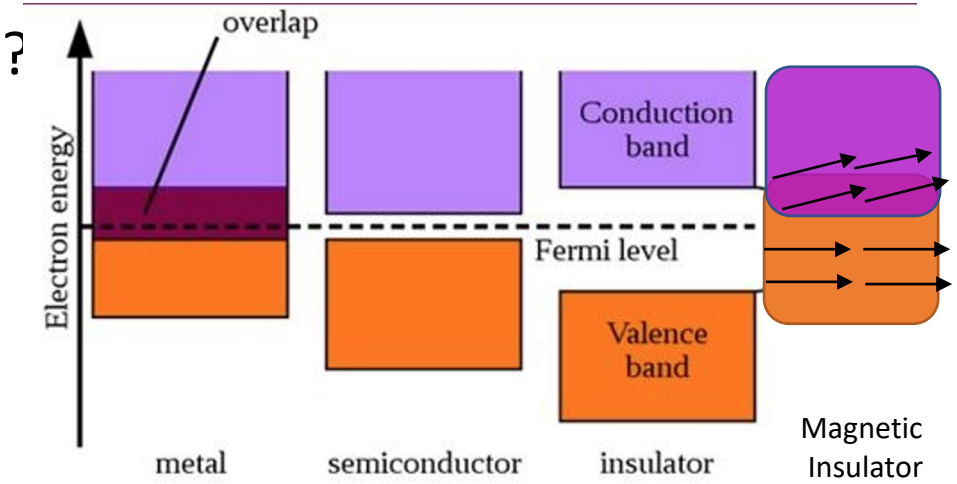
Repeated indices summed up

Completely Antisymmetric Tensor $\epsilon_{i_1 i_2 \ldots i_{N_e}} = \begin{cases} 1, & i_1 i_2 \ldots i_{N_e} \text{ is an even permutation of } 1\ 2\ 3\ \ldots N_e \\ -1, & i_1 i_2 \ldots i_{N_e} \text{ is an odd permutation of } 1\ 2\ 3\ \ldots N_e \\ 0, & \text{otherwise} \end{cases}$

Problems about Magnetism in Crystal Lattices of Insulators

First Problem: What is the **Magnetic Insulating States**?

Anderson: What is it that makes a material a magnetic insulator rather than a metal, a semiconductor or a superconductor ???

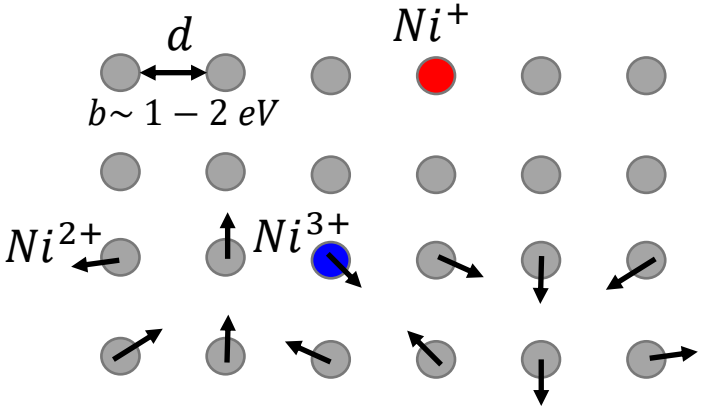


Answer:

1) Spin reorientations as Low-lying electronic excitation states

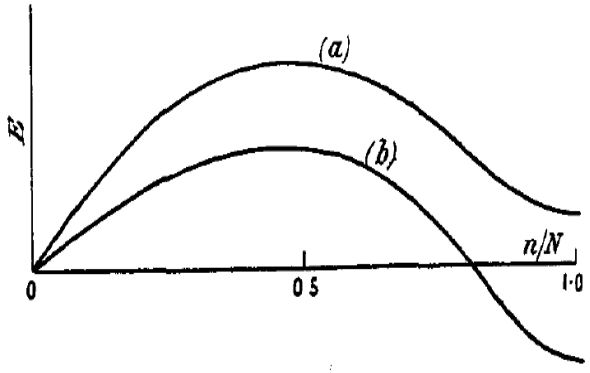
2) Mott Insulator b v.s. U

$$E_C(3d^7;3d^9) - E_C(3d^8;3d^8) = U \approx 5 - 15\ eV$$



Paramagnetic Cubic NiO

(a) Large d, $b < U$ (b) small d, $b > U$



Hypothetical plot of energy E against number n of pairs, (a) for large separations between atoms as in NiO, (b) for small separations as in metals.

Element	Symbol	Z	Electronic Configuration
Scandium	Sc	21	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^1\,4s^2$
Titanium	Ti	22	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^2\,4s^2$
Vanadium	V	23	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^3\,4s^2$
Chromium	Cr	24	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^1$
Manganese	Mn	25	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^5\,4s^2$
Iron	Fe	26	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^6\,4s^2$
Cobalt	Co	27	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^7\,4s^2$
Nickel	Ni	28	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^8\,4s^2$
Copper	Cu	29	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^1$
Zinc	Zn	30	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2$

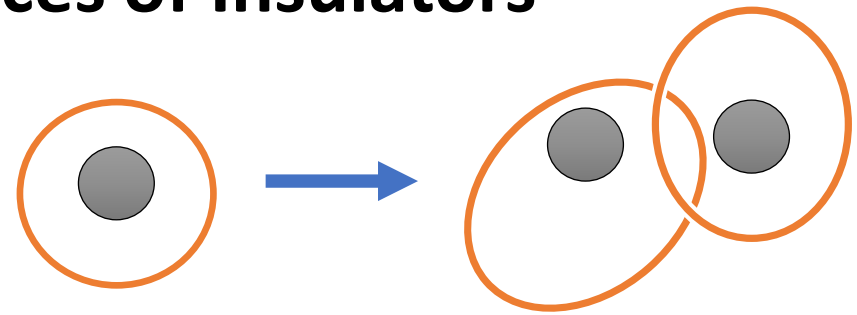
N F Mott 1949 Proc. Phys. Soc. A 62 416

Problems about Magnetism in Crystal Lattices of Insulators

Second Problem: Wavefunction Dilemma

(1) Orthogonality Dilemma: Overlap

(2) Modified Wavefunction in a crystal

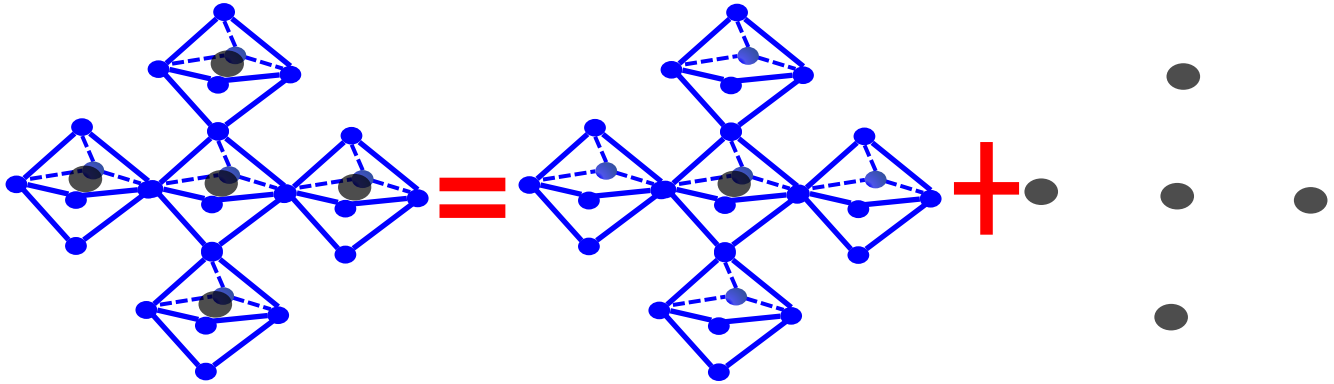


Isolated ion orbital In Crystal

Way out:

(1) Ligand Field Theory Aspect

(2) How magnetic ion interact with each in lattice



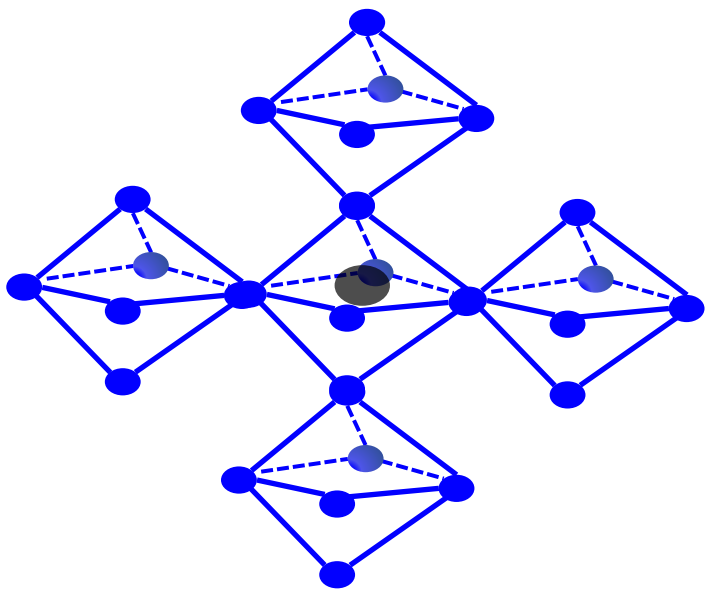
Magnetic ion Ligand ion

Conclusion	Experimental Results	References
Ligand field wavefunction undisturbed by other magnetic ions	Agreement of Hyperfine interaction with ligand ion nuclei between dilute and concentrated versions of the same salts and between paramagnetic and AFM temperature regions	*R. G. Shulman and V. Jaccarino, Phys. Rev. 103, 1126 (1956); 107, 1196 (1957); 108, 1219 (1957)* *A.M.Clogston, et al, Phys. Rev. 117, 1222 (1960)*
Well-defined energy level and wavefunction belonging to each magnetic ion, not changed by other magnetic ion	Agreement of crystal field parameters and exchange integrals in concentrated and dilute systems	J.H.E.Griffiths, et al, Proc. Roy. Soc. A250, 84 (1959) J.W.Stout, J. Chem. Phys. 31, 709(1959)

P. W. Anderson, Phys. Rev. 115, 2 (1959)

Theoretical Frame for Magnetism of Insulators

Ligand Field Theory Aspect



Nonmagnetic electrons

(1) As known core electrons unchanged by  interaction

(2) Contribute to the self-consistent field with wavefunction orthogonal to that of magnetic ions

(3) **Make partial covalent bond with $3d$ functions: anti-bonding**

Solution : Full Many-body Method or Band Theory + Hartree-Fock Method

One-electron Problem + Coulomb Correlation

$$\frac{p^2}{2m}\psi_k(r) + V(r)\psi_k(r) + \left[\sum_j^{N_e}\int dr_j\, v_{ij}\left|\psi_j(r_j)\right|^2\right]\psi_k(r) - \sum_j^{N_e}\sum_{\sigma_j}^{\pm 1}\int dr_j\, \psi_j^{\dagger}(r_j,\sigma_j)\psi_k(r_j,\sigma_j)v_{ij}\psi_j(r) = \epsilon(k)\psi_k(r)$$

$$\psi_k(r) = e^{ik\cdot r}u_k(r) \qquad u_k(r+R) = u_k(r)$$

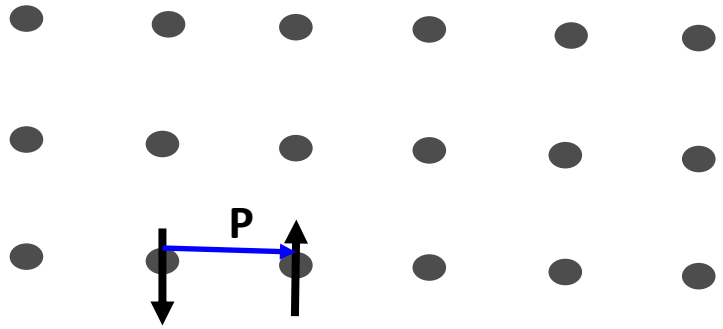
Wannier Functions

To each d band "m", $H_{sc}\psi_k^m(r) = \epsilon_m(k)\,\psi_k^m(r)$ $\quad \epsilon_m(k) = c_m + \sum_R b_m(R)e^{ik\cdot R}$ $\quad a_m(r-R) = \frac{1}{\sqrt{N}}\sum_k e^{ik\cdot R}\psi_k^m(r)$

$$H_{sc}a_m(r-R) = c_m a_m(r-R) + \sum_S b_m(S)a_m(r-R-S) \qquad H_{sc}a_m(r-R) = c_m a_m(r-R) + \sum_{m',P} b_{mm'}(P)a_{m'}(r-R-P)$$

Theoretical Frame for Magnetism of Insulators

Interactions Between Magnetic Electrons



$|\downarrow\rangle|\uparrow\rangle \longrightarrow |\downarrow\uparrow\rangle|0\rangle$ Or $|0\rangle|\downarrow\uparrow\rangle$

(1) On the same ion core

(1.1) Coulomb Repulsion: U

(1.2) True exchange energy for parallel spin: $J_{mm'}$

(1.3) Relative orientations of the orbits contribute to U

(2) On different ions: Exchange Effects

Direct exchange ,Superexchange, Double Exchange, Indirect and Polarization Effect.

$$a_m(\boldsymbol{r}-\boldsymbol{R}) \to a_m(\boldsymbol{r}-\boldsymbol{R}) + \sum_{m'} \frac{b_{mm'}(\boldsymbol{P})}{U} a_{m'}(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{P})$$

$$a_{m'}(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{P}) \to a_{m'}(\boldsymbol{r}-\boldsymbol{R}-\boldsymbol{P}) + \sum_{m'} \frac{b_{mm'}(\boldsymbol{P})}{U} a_m(\boldsymbol{r}-\boldsymbol{R})$$

$$\Delta E(parallel - antiparallel) = -\frac{b^2}{E(|\downarrow\uparrow\rangle|0\rangle) - E(|\downarrow\rangle|\uparrow\rangle)}$$

$$-\frac{b^2}{E(|0\rangle|\downarrow\uparrow\rangle) - E(|\downarrow\rangle|\uparrow\rangle)} = -\frac{2b^2}{U}$$

$$\Delta E = \sum_{m,m',\boldsymbol{R},\boldsymbol{P}} \frac{|b_{mm'}(\boldsymbol{P})|^2}{U}\left(-\frac{1}{2} + 2\boldsymbol{s}_{\boldsymbol{R}}^{\boldsymbol{m}} \cdot \boldsymbol{s}_{\boldsymbol{R}+\boldsymbol{P}}^{m'}\right)$$

$$E(|0\rangle|\downarrow\uparrow\rangle) - E(|\downarrow\rangle|\uparrow\rangle) = E(|\downarrow\uparrow\rangle|0\rangle) - E(|\downarrow\rangle|\uparrow\rangle) = U$$

Supplementary Materials

Permutation Symmetry for Many-body System

(0) $\mathbb{P}|q\rangle = |\mathbb{P}q\rangle \qquad |q\rangle \equiv |q_1, q_2, \dots, q_N\rangle \qquad \int dq|q\rangle\langle q| = 1$

$\Psi(q) \equiv \langle q|\Psi\rangle$

(1) $\forall\ |q\rangle$ and $|\Psi\rangle$

$$\left\langle \mathbb{P}^\dagger q \middle| \Psi \right\rangle = \langle q|\mathbb{P}|\Psi\rangle = \int dq'\langle q|\mathbb{P}|q'\rangle\langle q'|\Psi\rangle = \int dq'\langle q|\mathbb{P}q'\rangle\Psi(q') = \Psi(\mathbb{P}^{-1}q) = \langle \mathbb{P}^{-1}q|\Psi\rangle$$

$$\Longrightarrow \mathbb{P}^\dagger = \mathbb{P}^{-1}$$

(2) If $|\Psi\rangle = |q'\rangle, \langle q|\mathbb{P}|q'\rangle = \langle q|\mathbb{P}q'\rangle = \boldsymbol{\delta(q - \mathbb{P}q') = \delta(\mathbb{P}^{-1}q - q')} = \langle \mathbb{P}^{-1}q|q'\rangle$

(3) $\langle q|H|q'\rangle = \langle \mathbb{P}q|H|\mathbb{P}q'\rangle = \left\langle q \middle| \mathbb{P}^{-1}H\mathbb{P} \middle| q'\right\rangle \Longrightarrow \boldsymbol{H} = \mathbb{P}^{-1}H\mathbb{P}$ or $H\mathbb{P} = \mathbb{P}H$ **A constant of motion**

(4) Casimir operator:

real variables $\chi_c = \frac{\sum_{i=1}^{n_c} P_i}{n_c}$, where $P_i \epsilon$ Class c, or $\chi_c = \frac{\sum_{i=1}^{n} P_c P_i {P_c}^{-1}}{n}$, where $P_c \epsilon$ Class c,

$P_i \epsilon$ All Permutations, $n = N!$

Suppose there are m classes, then they correspond to m Casimir operators : $\chi_1, \chi_2, \dots, \chi_m$, which are absolute constants of motion and whose eigenvalues can be used to label stationary states.

P.A.M.Dirac, Proc.Roy.Soc. A123, 714 (1929)

Wannier Function: *from Bloch states to local orbitals*

Periodicity of crystal lattice: $$\psi_{m,\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{j=1}^{N} a_m(R_j,\vec{r})e^{i\vec{k}\cdot\vec{R}_j}$$

Localized orbitals as Wannier function: $$a_m(R_j,\vec{r}) = \frac{1}{\sqrt{N}}\sum_{\vec{k}} \psi_{m,\vec{k}}(\vec{r})e^{-i\vec{k}\cdot\vec{R}_j}$$

1. $a_m(R_j,\vec{r}) = a_m(\vec{r}-R_j)$**, i.e.** $\forall$ **lattice vector** R_n, $a_m(R_j,\vec{r}) = a_m(R_j+R_n,\vec{r}+R_n)$

$Hint$: $\psi_{\varepsilon,\vec{k}}(\vec{r}+R_n) = e^{i\vec{k}\cdot R_n}\psi_{\varepsilon,\vec{k}}(\vec{r})$;

2. An orthonormal basis: $$\int d^3r\, a_m{}^*(R_k,\vec{r})a_m(R_j,\vec{r}) = \delta_{R_k,R_j}$$

3. Since Bloch states defined up to an overall phase $\psi_{m,\vec{k}}(\vec{r}) \to e^{i\theta}\psi_{m,\vec{k}}(\vec{r})$**, Wannier function can be chosen as the maximally-localized set:** $a_m(R_j,\vec{r})$ **localized around** R_j **and rapidly goes to zero away from** R_j**. For 1-dimension and potentially separable cases in higher dimensions, the maximally-localized set is unique.**[4]

Variational Calculation for H-F Method

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle = \left\langle \Psi \middle| \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij} \middle| \Psi \right\rangle = \sum_{i=1}^{N_e} \langle \Psi | h_i | \Psi \rangle + \sum_{i>j}^{N_e} \langle \Psi | v_{ij} | \Psi \rangle$$

$$\langle \Psi | h_k | \Psi \rangle = \int dr_1 dr_2 \dots dr_{N_e} \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \psi_{i_1}^\dagger(r_1, \sigma_1) \psi_{i_2}^\dagger(r_2, \sigma_2) \dots \psi_{i_{N_e}}^\dagger(r_{N_e}, \sigma_{N_e}) h_k \epsilon_{j_1 j_2 \dots j_{N_e}} \psi_{j_1}(r_1, \sigma_1)\, \psi_{j_2}(r_2, \sigma_2)$$

$$\dots \psi_{j_{N_e}}(r_{N_e}, \sigma_{N_e}) = \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \left[\int dr_1\, \psi_{i_1}^\dagger(r_1, \sigma_1) \psi_{j_1}(r_1, \sigma_1) \right] \dots \left[\int dr_k\, \psi_{i_k}^\dagger(r_k, \sigma_k) h_k \psi_{j_k}(r_k, \sigma_k) \right] \dots$$

$$\left[\int dr_{N_e}\, \psi_{i_{N_e}}^\dagger(r_{N_e}, \sigma_{N_e}) \psi_{j_{N_e}}(r_{N_e}, \sigma_{N_e}) \right] = \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \langle \psi_{i_1} | \psi_{j_1} \rangle \dots \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle \dots \left\langle \psi_{i_{N_e}} \middle| \psi_{j_{N_e}} \right\rangle$$

$$= \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \delta_{i_1 j_1} \dots \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle \dots \delta_{i_{N_e} j_{N_e}} = \frac{1}{N_e!} \epsilon_{i_1 \dots i_k \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots i_{N_e}} \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle$$

$$= \sum_{i_k, j_k = 1}^{N_e} (N_e - 1)!\ \delta_{i_k j_k} \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle = \sum_{i_k}^{N_e} \frac{1}{N_e} \langle \psi_{i_k} | h_k | \psi_{i_k} \rangle = \frac{1}{N_e} N_e \langle \psi_k | h_k | \psi_k \rangle = \langle \psi_k | h_k | \psi_k \rangle$$

$$\epsilon_{i_1 \dots i_k \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots i_{N_e}} = \sum_{i_k, j_k = 1}^{N_e} (N_e - 1)!\, \epsilon_{123 \dots (N_e - 1)}{}^2 \delta_{i_k j_k} = \sum_{i_k, j_k = 1}^{N_e} (N_e - 1)!\ \delta_{i_k j_k}$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle = \left\langle \Psi \middle| \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij} \middle| \Psi \right\rangle = \sum_{i=1}^{N_e} \langle \Psi | h_i | \Psi \rangle + \sum_{i>j}^{N_e} \langle \Psi | v_{ij} | \Psi \rangle$$

$$\langle \Psi | v_{km} | \Psi \rangle = \int dr_1 dr_2 \dots dr_{N_e} \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \psi_{i_1}^\dagger(r_1,\sigma_1) \psi_{i_2}^\dagger(r_2,\sigma_2) \dots \psi_{i_{N_e}}^\dagger(r_{N_e},\sigma_{N_e}) v_{km} \epsilon_{j_1 j_2 \dots j_{N_e}} \psi_{j_1}(r_1,\sigma_1)$$

$$\psi_{j_2}(r_2,\sigma_2) \dots \psi_{j_{N_e}}(r_{N_e},\sigma_{N_e}) = \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \left[\int dr_1\, \psi_{i_1}^\dagger(r_1,\sigma_1) \psi_{j_1}(r_1,\sigma_1) \right] \dots$$

$$\left[\int dr_k\, dr_m \psi_{i_k}^\dagger(r_k,\sigma_k) \psi_{i_m}^\dagger(r_m,\sigma_m) v_{km} \psi_{j_k}(r_k,\sigma_k) \psi_{j_m}(r_m,\sigma_m) \right] \dots \left[\int dr_{N_e}\, \psi_{i_{N_e}}^\dagger(r_{N_e},\sigma_{N_e}) \psi_{j_{N_e}}(r_{N_e},\sigma_{N_e}) \right]$$

$$= \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \langle \psi_{i_1} | \psi_{j_1} \rangle \dots \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle \dots \left\langle \psi_{i_{N_e}} \middle| \psi_{j_{N_e}} \right\rangle$$

$$= \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \delta_{i_1 j_1} \dots \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle \dots \delta_{i_{N_e} j_{N_e}} = \frac{1}{N_e!} \epsilon_{i_1 \dots i_k, \dots i_m \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots j_m \dots i_{N_e}} \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle$$

$$= \sum_{i_k \neq i_m, j_k \neq j_m}^{N_e} \frac{1}{N_e(N_e-1)} \left(\delta_{i_k j_k} \delta_{i_m j_m} - \delta_{i_k j_m} \delta_{i_m j_k} \right) \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle$$

$$= \sum_{i_k \neq i_m}^{N_e} \frac{1}{N_e(N_e-1)} \left[\langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{i_k} \psi_{i_m} \rangle - \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{i_m} \psi_{i_k} \rangle \right] = \langle \psi_k \psi_m | v_{km} | \psi_k \psi_m \rangle - \langle \psi_k \psi_m | v_{km} | \psi_m \psi_k \rangle$$

$$\epsilon_{i_1 \dots i_k, \dots i_m \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots j_m \dots i_{N_e}} = \sum_{i_k \neq i_m, j_k \neq j_m}^{N_e} (N_e - 2)!\, \epsilon_{123 \dots (N_e-2)}{}^2 \left(\delta_{i_k j_k} \delta_{i_m j_m} - \delta_{i_k j_m} \delta_{i_m j_k} \right) = \sum_{i_k \neq i_m, j_k \neq j_m}^{N_e} (N_e - 2)!\, \left(\delta_{i_k j_k} \delta_{i_m j_m} - \delta_{i_k j_m} \delta_{i_m j_k} \right)$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle = \left\langle \Psi \middle| \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij} \middle| \Psi \right\rangle = \sum_{i=1}^{N_e} \langle \Psi | h_i | \Psi \rangle + \sum_{i>j}^{N_e} \langle \Psi | v_{ij} | \Psi \rangle$$

$$= \sum_{k=1}^{N_e} \langle \psi_k | h_k | \psi_k \rangle + \sum_{k>m}^{N_e} [\langle \psi_k \psi_m | v_{km} | \psi_k \psi_m \rangle - \langle \psi_k \psi_m | v_{km} | \psi_m \psi_k \rangle]$$

$$\langle \psi_k | h_k | \psi_k \rangle \equiv \int dr_k \, \psi_k^\dagger(r_k, \sigma_k) h_k \psi_k(r_k, \sigma_k)$$

$$\langle \psi_k \psi_m | v_{km} | \psi_k \psi_m \rangle \equiv \int dr_k \, dr_m |\psi_k(r_k, \sigma_k)|^2 v_{km} |\psi_m(r_m, \sigma_m)|^2$$

$$\langle \psi_k \psi_m | v_{km} | \psi_m \psi_k \rangle \equiv \int dr_k \, dr_m \psi_k^\dagger(r_k, \sigma_k) \psi_m^\dagger(r_m, \sigma_m) v_{km} \psi_m(r_k, \sigma_k) \psi_k(r_m, \sigma_m)$$

$$\mathcal{L}[\{\psi_i\}] \equiv E_e[\{\psi_i\}] - \sum_{i,j} \epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right) = \sum_{i=1}^{N_e} \langle \psi_i | h_i | \psi_i \rangle$$

$$+ \frac{1}{2} \sum_{i,j}^{N_e} [\langle \psi_i \psi_j | v_{ij} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | v_{ij} | \psi_j \psi_i \rangle] - \sum_{i,j} \epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right)$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$\mathcal{L}[\{\boldsymbol{\psi}_i\}] \equiv E_e[\{\boldsymbol{\psi}_i\}] - \sum_{i,j} \boldsymbol{\epsilon}_{ij} \left(\langle \boldsymbol{\psi}_i | \boldsymbol{\psi}_j \rangle - \boldsymbol{\delta}_{ij}\right) = \sum_{i=1}^{N_e} \langle \boldsymbol{\psi}_i | \boldsymbol{h}_i | \boldsymbol{\psi}_i \rangle$$

$$+ \frac{1}{2} \sum_{i,j}^{N_e} \left[\langle \boldsymbol{\psi}_i \boldsymbol{\psi}_j | \boldsymbol{v}_{ij} | \boldsymbol{\psi}_i \boldsymbol{\psi}_j \rangle - \langle \boldsymbol{\psi}_i \boldsymbol{\psi}_j | \boldsymbol{v}_{ij} | \boldsymbol{\psi}_j \boldsymbol{\psi}_i \rangle\right] - \sum_{i,j} \boldsymbol{\epsilon}_{ij} \left(\langle \boldsymbol{\psi}_i | \boldsymbol{\psi}_j \rangle - \boldsymbol{\delta}_{ij}\right)$$

$$\boldsymbol{\psi}_i^\dagger \to \boldsymbol{\psi}_i^\dagger + \boldsymbol{\delta}\boldsymbol{\psi}_i^\dagger$$

$$\delta\mathcal{L}[\{\boldsymbol{\psi}_i\}] = \sum_{i=1}^{N_e} \int d\boldsymbol{r}_i\, \delta\boldsymbol{\psi}_i^\dagger(\boldsymbol{r}_i) \boldsymbol{h}_i \boldsymbol{\psi}_i(\boldsymbol{r}_i) + \sum_{i}^{N_e} \int d\boldsymbol{r}_i\, \delta\boldsymbol{\psi}_i^\dagger(\boldsymbol{r}_i) \sum_{j}^{N_e} \int d\boldsymbol{r}_j\, \boldsymbol{\psi}_i(\boldsymbol{r}_i) \boldsymbol{v}_{ij} |\boldsymbol{\psi}_j(\boldsymbol{r}_j)|^2$$

$$- \sum_{i}^{N_e} \int d\boldsymbol{r}_i\, \delta\boldsymbol{\psi}_i^\dagger(\boldsymbol{r}_i, \boldsymbol{\sigma}_i) \sum_{j}^{N_e} \int d\boldsymbol{r}_j\, \boldsymbol{\psi}_j^\dagger(\boldsymbol{r}_j, \boldsymbol{\sigma}_j) \boldsymbol{v}_{ij} \boldsymbol{\psi}_j(\boldsymbol{r}_i, \boldsymbol{\sigma}_i) \boldsymbol{\psi}_i(\boldsymbol{r}_j, \boldsymbol{\sigma}_j) - \sum_{i=1}^{N_e} \int d\boldsymbol{r}_i\, \delta\boldsymbol{\psi}_i^\dagger(\boldsymbol{r}_i, \boldsymbol{\sigma}_i) \sum_{j}^{N_e} \boldsymbol{\epsilon}_{ij} \boldsymbol{\psi}_j(\boldsymbol{r}_i, \boldsymbol{\sigma}_i)$$

$$- \sum_{i,j} \delta\boldsymbol{\epsilon}_{ij} \left(\langle \boldsymbol{\psi}_i | \boldsymbol{\psi}_j \rangle - \boldsymbol{\delta}_{ij}\right) = \boldsymbol{0}$$

$$\boldsymbol{h}_i \boldsymbol{\psi}_i(\boldsymbol{r}_i, \boldsymbol{\sigma}_i) + \left[\sum_{j}^{N_e} \int d\boldsymbol{r}_j\, \boldsymbol{v}_{ij} |\boldsymbol{\psi}_j(\boldsymbol{r}_j, \boldsymbol{\sigma}_j)|^2\right] \boldsymbol{\psi}_i(\boldsymbol{r}_i, \boldsymbol{\sigma}_i) - \sum_{j}^{N_e} \int d\boldsymbol{r}_j\, \boldsymbol{\psi}_j^\dagger(\boldsymbol{r}_j, \boldsymbol{\sigma}_j) \boldsymbol{\psi}_i(\boldsymbol{r}_j, \boldsymbol{\sigma}_j) \boldsymbol{v}_{ij} \boldsymbol{\psi}_j(\boldsymbol{r}_i, \boldsymbol{\sigma}_i) - \sum_{j}^{N_e} \boldsymbol{\epsilon}_{ij} \boldsymbol{\psi}_j(\boldsymbol{r}_i, \boldsymbol{\sigma}_i) = \boldsymbol{0}$$

$$\langle \boldsymbol{\psi}_i | \boldsymbol{\psi}_j \rangle = \boldsymbol{\delta}_{ij} \qquad (1)$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

Similarly, $\boldsymbol{\psi_i \to \psi_i + \delta\psi_i}$ $\qquad \delta\mathcal{L}[\{\boldsymbol{\psi_i}\}] = 0$

$$\boldsymbol{h_i\psi_i(r_i) + \left[\sum_j^{N_e}\int dr_j\, v_{ij}|\psi_j(r_j,\sigma_j)|^2\right]\psi_i(r_i) - \sum_j^{N_e}\int dr_j\, \psi_j^\dagger(r_j,\sigma_j)\psi_i(r_j,\sigma_j)v_{ij}\psi_j(r_i) - \sum_j^{N_e}\epsilon_{ji}^*\psi_j(r_i,\sigma_i) = 0}$$

$$\boldsymbol{\langle\psi_i|\psi_j\rangle = \delta_{ij}}$$

(1)=(2) ➡ $\boldsymbol{\epsilon_{ji}^* = \epsilon_{ij}}$ **Self-adjoint or Hermitian**

∃ **Unitary transformation** $\boldsymbol{U, \psi_i \to \widetilde{\psi_i} = U_{ij}\psi_j}$ $\qquad \boldsymbol{\epsilon_{ij} \to \widetilde{\epsilon_{ij}} = U_{ik}\epsilon_{km}(U^{-1})_{mj} = \widetilde{\epsilon}_i\,\delta_{ij}}$ **Diagonalized!**

(1),(2) ➡ **Hartree-Fock Equation**

$$\boldsymbol{h_i\psi_i(r_i) + \left[\sum_j^{N_e}\int dr_j\, v_{ij}|\psi_j(r_j,\sigma_j)|^2\right]\psi_i(r_i) - \sum_j^{N_e}\int dr_j\, \psi_j^\dagger(r_j,\sigma_j)\psi_i(r_j)v_{ij}\psi_j(r_i,\sigma_i) = \epsilon_i\psi_i(r_i)}$$

For convenience, symbols $\widetilde{\psi_i}$ ***and*** $\widetilde{\epsilon_{ij}}$ ***have been changed back into*** ψ_i ***and*** ϵ_{ij}

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Koopmans Theorem

Born-Oppenheimer Approximation

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

A General Many-Body Problem:

1) N nuclei described by coordinates $\boldsymbol{R} \equiv \{\boldsymbol{R_1}, \boldsymbol{R_2}, \dots, \boldsymbol{R_N}\}$, momenta $\boldsymbol{P} \equiv \{\boldsymbol{P_1}, \boldsymbol{P_2}, \dots, \boldsymbol{P_N}\}$ and masses $\{\boldsymbol{M_1}, \boldsymbol{M_2}, \dots, \boldsymbol{M_N}\}$
2) N_e electrons described by coordinates $\boldsymbol{r} \equiv \{\boldsymbol{r_1}, \boldsymbol{r_2}, \dots, \boldsymbol{r_{N_e}}\}$, momenta $\boldsymbol{p} \equiv \{\boldsymbol{p_1}, \boldsymbol{p_2}, \dots, \boldsymbol{p_{N_e}}\}$, spins $\boldsymbol{s} \equiv \{\boldsymbol{s_1}, \boldsymbol{s_2}, \dots, \boldsymbol{s_{N_e}}\}$ and masses $\{\boldsymbol{m_1}, \boldsymbol{m_2}, \dots, \boldsymbol{m_{N_e}}\}$
3) Hamiltonian: $\boldsymbol{H = T_N(R) + T_e(r) + V_{NN}(R) + V_{eN}(r, R) + V_{ee}(r)}$

Where nuclei's kinetic energy $T_N(\boldsymbol{R}) \equiv \sum_{I=1}^{N} \frac{\boldsymbol{P_I^2}}{2M_I}$; Electrons' kinetic energy $T_e(\boldsymbol{r}) \equiv \sum_{i=1}^{N_e} \frac{\boldsymbol{p_i^2}}{2m_i}$

Nucleus-nucleus Coulomb Potential $V_{NN}(\boldsymbol{R}) \equiv \frac{1}{2}\sum_{I,J}^{N} \frac{Z_I Z_J e^2}{|\boldsymbol{R_I} - \boldsymbol{R_J}|} = \sum_{I>J}^{N} \frac{Z_I Z_J e^2}{|\boldsymbol{R_I} - \boldsymbol{R_J}|}$ *$Z_I e$: the charge of the nucleus located at $\boldsymbol{R_I}$*

Nucleus- electron Coulomb Potential $V_{eN}(\boldsymbol{r}, \boldsymbol{R}) \equiv -\sum_{I,i}^{N.N_e} \frac{Z_I e^2}{|\boldsymbol{R_I} - \boldsymbol{r_i}|}$

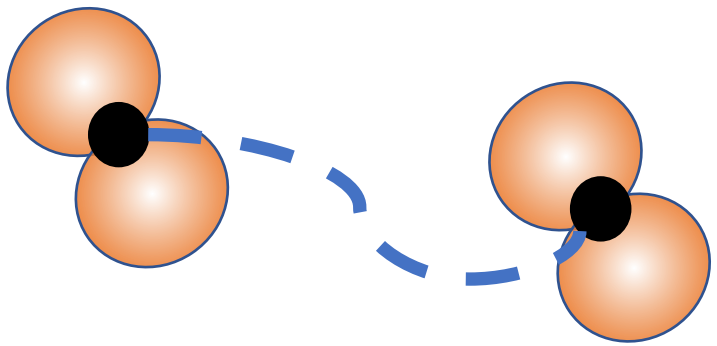
Electron- electron Coulomb Potential $V_{ee}(\boldsymbol{r}) \equiv \frac{1}{2}\sum_{i,j}^{N_e} \frac{e^2}{|\boldsymbol{r_i} - \boldsymbol{r_j}|} = \sum_{i>j}^{N_e} \frac{e^2}{|\boldsymbol{r_i} - \boldsymbol{r_j}|}$

Impossible to solve directly when $N, N_e \gg 1$!

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

Approximations:

1) **Born-Oppenheimer Approximation**
2) **Hartree-Fock Approximation**



$\frac{m_e}{M_n} < 10^{-2} \ll 1$ ➡ Electrons motion time scare $\ll$ Nuclei motion time scale

➡ **1. (1.1)Electrons follow the nuclear motion adiabatically and are dragged by the nuclei without a finite relaxation time; (1.2)Electronic wave function depends on the nuclear positions but not their velocities**

2. (2.1)Nuclear wave functions are relatively spatially localized and more like a point classical particle; (2.2) The nuclear motion sees a smeared-out potential from the speedy electrons

$$H(r,R) = H_e(r,R) + H_N(R);\ H_e(r,R) \equiv T_e(r) + V_{eN}(r,R) + V_{ee}(r), H_N(R) \equiv T_N(R) + V_{NN}(R)$$

$$H(r,R)\Psi(r,R) = E_{tot}\Psi(r,R) \quad \Psi(r,R) \equiv \phi_e(r,R)\phi_N(R) \quad H_e(r,R)\phi_e(r,R) = E_e\phi_e(r,R)$$

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

$$H(r,R)\Psi(r,R) = E_{tot}\Psi(r,R) \qquad \Psi(r,R) \equiv \phi_e(r,R)\phi_N(R) \qquad H_e(r,R)\phi_e(r,R) = E_e\phi_e(r,R)$$

$$H_N(R)\phi_N(R) = (E_{tot} - E_e)\phi_N(R) \quad \Leftrightarrow \quad \phi_e(r,R)H_N(R)\phi_N(R) = (E_{tot} - E_e)\Psi(r,R)$$

$$\Leftrightarrow \quad \phi_e(r,R)H_N(R)\phi_N(R) = \big(H(r,R) - H_e(r,R)\big)\Psi(r,R) = H_N(R)\phi_e(r,R)\phi_N(R)$$

$$\Leftrightarrow \quad T_N(R)\phi_e(r,R)\phi_N(R) = \phi_e(r,R)T_N(R)\phi_N(R) \qquad H_N(R)\phi_e(r,R)\phi_N(R) = (T_N(R) + V_{NN}(R))\phi_e(r,R)\phi_N(R)$$

$$\Leftrightarrow \quad -\hbar^2\sum_{I=1}^{N}\frac{\nabla_I^2}{2M_I}\phi_e(r,R)\phi_N(R) = -\hbar^2\sum_{I=1}^{N}\frac{1}{2M_I}\left[\phi_N(R)\nabla_I^2\phi_e(r,R) + 2\nabla_I\phi_e(r,R)\nabla_I\phi_N(R) + \phi_e(r,R)\nabla_I^2\phi_N(R)\right]$$

$$= -\hbar^2\sum_{I=1}^{N}\frac{1}{2M_I}\phi_e(r,R)\nabla_I^2\phi_N(R)$$

$$\Leftrightarrow \quad -\hbar^2\sum_{I=1}^{N}\frac{1}{2M_I}\left[\phi_N(R)\nabla_I^2\phi_e(r,R) + 2\nabla_I\phi_e(r,R)\nabla_I\phi_N(R)\right] = 0$$

Born-Oppenheimer Approximation

$$\left|\frac{-\hbar^2}{2M_I}\nabla_I^2\phi_e(r,R)\right| \approx \left|\frac{-\hbar^2}{2M_I}\nabla_r^2\phi_e(r,R)\right| \approx \left|\frac{m_e}{M_I}\frac{p_e^2}{2m_e}\right| \ll \left|\frac{p_e^2}{2m_e}\right|$$

$$\left|\frac{-\hbar^2}{M_I}\nabla_I\phi_e(r,R)\nabla_I\phi_N(R)\right| \approx \left|\frac{-\hbar^2}{M_I}\nabla_r\phi_e(r,R)\nabla_I\phi_N(R)\right| \approx \left|\frac{P_I}{M_I}p_e\right| \ll \left|\frac{{p_e}^2}{m_e}\right|$$

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

Conclusion:

$$\boxed{H(r,R)\Psi(r,R) = E_{tot}\Psi(r,R)} \approx$$

$$\Psi(r,R) \equiv \phi_e(r,R)\phi_N(R)$$

$$\boxed{H_e(r,R)\phi_e(r,R) = E_e\phi_e(r,R)}$$

$$H_N(R)\phi_N(R) = (E_{tot} - E_e)\phi_N(R)$$

$$H_e(r,R) \equiv T_e(r) + V_{eN}(r,R) + V_{ee}(r),$$

$$H_N(R) \equiv T_N(R) + V_{NN}(R)$$

$$T_N(R) \equiv \sum_{I=1}^{N} \frac{P_I^2}{2M_I}; \qquad T_e(r) \equiv \sum_{i=1}^{N_e} \frac{p_i^2}{2m_i}$$

$$V_{NN}(R) \equiv \frac{1}{2}\sum_{I,J}^{N} \frac{Z_I Z_J e^2}{|R_I - R_J|} = \sum_{I>J}^{N} \frac{Z_I Z_J e^2}{|R_I - R_J|}$$

$$V_{eN}(r,R) \equiv -\sum_{I,i}^{N.N_e} \frac{Z_I e^2}{|R_I - r_i|}$$

$$V_{ee}(r) \equiv \frac{1}{2}\sum_{i,j}^{N_e} \frac{e^2}{|r_i - r_j|} = \sum_{i>j}^{N_e} \frac{e^2}{|r_i - r_j|}$$

Born-Oppenheimer Approximation: Electronic Berry Connection