Quantum Physics Exercise Class IV

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General formulation of time–independent perturbation theory

- Question: Perturbatively solve the eigenequation of Hamiltonian $\hat{H} = \hat{H}_0 + \lambda\hat{H}_1$ with

$$\hat{H}_0|k\alpha\rangle = \epsilon_k|k\alpha\rangle \ (\alpha = 1, 2, \cdots, \dim\mathcal{H}_k) \tag{1}$$

  The total Hilbert space is given by $\mathcal{H} = \sum_k \oplus\mathcal{H}_k$.

- Separate: $\mathcal{H} = \mathcal{H}_n \oplus \mathcal{H}_n^\perp$. Define the projection operators:

$$\hat{P}_n \equiv \sum_\alpha |n\alpha\rangle\langle n\alpha| \tag{2}$$

$$\hat{Q}_n \equiv 1 - \hat{P}_n = \sum_{\substack{k\neq n \\ \alpha}} |k\alpha\rangle\langle k\alpha| \tag{3}$$

  And define the resolvent operator:

$$\hat{R}_n \equiv \sum_{\substack{k\neq n \\ \alpha}} \frac{|k\alpha\rangle\langle k\alpha|}{E_n - \epsilon_k} \tag{4}$$

  with E_n being the n-th eigenvalue of $\hat{H}$.

- Properties:

$$\hat{P}_n\hat{R}_n = \hat{R}_n\hat{P}_n = 0, \ \hat{Q}_n\hat{R}_n = \hat{R}_n\hat{Q}_n = \hat{R}_n, \ \hat{R}_n(E_n - \hat{H}_0) = (E_n - \hat{H}_0)\hat{R}_n = \hat{Q}_n \tag{5}$$

General formulation of time–independent perturbation theory

- Then

$$\hat{Q}_n|\Psi_n\rangle = \hat{R}_n(E_n - \hat{H}_0)|\Psi_n\rangle = \lambda\hat{R}_n\hat{H}_1|\Psi_n\rangle \tag{6}$$

On the other hand,

$$\hat{Q}_n|\Psi_n\rangle = (1 - \hat{P}_n)|\Psi_n\rangle \tag{7}$$

- Therefore,

$$|\Psi_n\rangle = (1 - \lambda\hat{R}_n\hat{H}_1)^{-1}\hat{P}_n|\Psi_n\rangle = \sum_{j=0}^{\infty}\lambda^j(\hat{R}_n\hat{H}_1)^j\hat{P}_n|\Psi_n\rangle \tag{8}$$

Nondegenerate case

- Normalization:

$$\hat{P}_n|\Psi_n\rangle \equiv |n\rangle \tag{9}$$

- Then

$$|\Psi_n\rangle = |n\rangle + \lambda \sum_{\substack{k\neq n\\ \alpha}} \frac{|k\alpha\rangle\langle k\alpha|\hat{H}_1|n\rangle}{E_n - \epsilon_k} + \lambda^2 \sum_{\substack{k\neq n\\ \alpha}} \sum_{\substack{k'\neq n\\ \alpha'}} \frac{|k\alpha\rangle\langle k\alpha|\hat{H}_1|k\beta\rangle\langle k\beta|\hat{H}_1|n\rangle}{(E_n - \epsilon_k)(E_n - \epsilon'_k)} + \cdots \tag{10}$$

- By using $E_n - \epsilon_n = \lambda\langle n|\hat{H}_1|\Psi_n\rangle$, we have

$$\begin{aligned} E_n = \epsilon_n + \lambda\langle n|\hat{H}_1|n\rangle + \lambda^2 \sum_{\substack{k\neq n\\ \alpha}} \frac{|\langle k\alpha|\hat{H}_1|n\rangle|^2}{E_n - \epsilon_k} \\ + \lambda^3 \sum_{\substack{k\neq n\\ \alpha}} \sum_{\substack{k'\neq n\\ \alpha'}} \frac{\langle n|\hat{H}_1|k\alpha\rangle\langle k\alpha|\hat{H}_1|k\beta\rangle\langle k\beta|\hat{H}_1|n\rangle}{(E_n - \epsilon_k)(E_n - \epsilon'_k)} + \cdots \end{aligned} \tag{11}$$

Nondegenerate case (**important**)

- Up to $\mathcal{O}(\lambda)$,

$$E_n = \epsilon_n + \lambda\langle n|\hat{H}_1|n\rangle + \mathcal{O}(\lambda^2) \tag{12}$$

and

$$|\Psi_n\rangle = |n\rangle + \lambda \sum_{\substack{k\neq n \\ \alpha}} \frac{|k\alpha\rangle\langle k\alpha|\hat{H}_1|n\rangle}{\epsilon_n - \epsilon_k} \tag{13}$$

- Up to $\mathcal{O}(\lambda^2)$,

$$E_n = \epsilon_n + \lambda\langle n|\hat{H}_1|n\rangle + \lambda^2 \sum_{\substack{k\neq n \\ \alpha}} \frac{|\langle k\alpha|\hat{H}_1|n\rangle|^2}{\epsilon_n - \epsilon_k} + \mathcal{O}(\lambda^3) \tag{14}$$

Degenerate case

- Let

$$\hat{P}_n|\Psi_n\rangle \equiv \sum_{\alpha} c_\alpha |n\alpha\rangle \tag{15}$$

- Then recall

$$\langle n\alpha|\hat{P}_n|\Psi_n\rangle = \langle n\alpha|\Psi_n\rangle = c_\alpha \tag{16}$$

and we have

$$\begin{aligned}(E_n - \epsilon_n)c_\alpha &= \lambda\langle n\alpha|\hat{H}_1|\Psi_n\rangle \\ &= \sum_{\beta}\left[\lambda\langle n\alpha|\hat{H}_1|n\beta\rangle + \lambda^2 \sum_{\substack{k\neq n,\\ \gamma}} \frac{\langle n\alpha|\hat{H}_1|k\gamma\rangle\langle k\gamma|\hat{H}_1|n\beta\rangle}{E_n - \epsilon_k} + \cdots\right]c_\beta\end{aligned} \tag{17}$$

- Up to the first order,

$$(E_n - \epsilon_n)c_\alpha = \lambda\sum_{\beta}\langle n\alpha|\hat{H}_1|n\beta\rangle c_\beta \tag{18}$$

The solution gives

$$E_{n\alpha}^{(1)} = \epsilon_n + \lambda\epsilon_{n\alpha}^{(1)} \tag{19}$$

with $\epsilon_{n\alpha}^{(1)}$ being the α-th eigenvalue of $\langle n\alpha|\hat{H}_1|n\beta\rangle$.

Degenerate case

- The eigenequation also gives the eigenvectors:

$$|\widetilde{n\alpha}\rangle \equiv \sum_{\beta} c_\beta |n\beta\rangle \tag{20}$$

satisfying

$$\hat{H}_1|\widetilde{n\alpha}\rangle = \epsilon_{n\alpha}^{(1)}|\widetilde{n\alpha}\rangle \text{ (only valid in } \mathcal{H}_n \text{ space)} \tag{21}$$

and $\langle n'\beta|\widetilde{n\alpha}\rangle = 0 \ (n \neq n')$.

- Project:

$$\hat{P}_{n\alpha}|\Psi_{n\alpha}\rangle = |\widetilde{n\alpha}\rangle \tag{22}$$

- Then

$$E_{n\alpha} - \epsilon_n = \lambda\langle\widetilde{n\alpha}|\hat{H}_1|\Psi_{n\alpha}\rangle \tag{23}$$

- This leads to

$$E_{n\alpha} = \epsilon_n + \lambda\epsilon_{n\alpha}^{(1)} + \lambda^2 \sum_{\substack{k\neq n \\ \gamma}} \frac{\langle\widetilde{n\alpha}|\hat{H}_1|k\gamma\rangle\langle k\gamma|\hat{H}_1|\widetilde{n\alpha}\rangle}{\epsilon_n - \epsilon_k} + \mathcal{O}(\lambda^3) \tag{24}$$

Variational principle (**important**)

Given a trial state $|\Psi\rangle$ satisfying the boundary conditions, there exists

$$\frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \geq E_0 \tag{25}$$

with E_0 being the ground state energy of H. In practice, we assume the trial wave function parameterized by $\{\lambda_i\}$, denoted as $\Psi(x; \{\lambda_i\})$. The we evaluate the expectation value,

$$E(\{\lambda_i\}) \equiv \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{26}$$

Then minimize it by

$$\frac{\partial}{\partial\lambda_i} E(\{\lambda_i\}) = 0 \tag{27}$$

and we obtain the estimated ground state energy $\tilde{E}_0$.

Variational principle

In general, the energy is a functional with the form

$$E[\{\psi_i\}] = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle} \tag{28}$$

The minimize goes by

$$\frac{\delta}{\delta\psi_i}E[\{\psi_i\}] = 0 \tag{29}$$

In some cases, the normalization is not convenient to do. We can alternatively adopt the Lagrangian multiplier method, that is,

$$E[\{\psi_i\},\beta] = \langle\Psi|H|\Psi\rangle - \beta(\langle\Psi|\Psi\rangle - 1) \tag{30}$$

Functional calculus

- Consider a multi-variable function $F(\phi_1, \cdots, \phi_n)$ with $\phi_i \equiv \phi(x_i)$ and $x_i \in (a, b)$. When $n \to \infty$, we define the functional

$$F(\phi_1, \cdots, \phi_n) \longrightarrow F[\phi(x)] \tag{31}$$

- Similarly,

$$F(\phi_1, \cdots, \phi_n) = \sum_{m=0}^{\infty} \frac{1}{m!} \sum_{i_1} \cdots \sum_{i_m} \frac{\partial^m F}{\partial \phi_{i_1} \cdots \partial \phi_{i_m}} \bigg|_0 \phi_{i_1} \cdots \phi_{i_m} \tag{32}$$

has a functional form

$$F[\phi] = \sum_{m=0}^{\infty} \frac{1}{m!} \int \cdots \int \mathrm{d}x_1 \cdots \mathrm{d}x_m \, \frac{\delta^m F}{\delta \phi(x_1) \cdots \delta \phi(x_m)} \bigg|_0 \phi(x_1) \cdots \phi(x_m) \tag{33}$$

Functional calculus

- The functional differential is defined through

$$\delta F[\phi] = F[\phi + \delta\phi] - F[\phi] = \int \mathrm{d}x\, A[\phi, x]\delta\phi(x) \tag{34}$$

and

$$A[\phi, x] \equiv \frac{\delta F[\phi]}{\delta\phi(x)} = \lim_{h\to 0} \frac{1}{h}\Big(F[\phi(u) + h\delta(x-u)] - F[\phi(u)]\Big) \tag{35}$$

- Newton–Leibniz formula:

$$\frac{\delta}{\delta\phi}(F[\phi]G[\phi]) = \frac{\delta F[\phi]}{\delta\phi}G[\phi] + F[\phi]\frac{\delta G[\phi]}{\delta\phi} \tag{36}$$

- Chain's rule:

$$\frac{\delta}{\delta\phi}F[G[\phi]] = \int \mathrm{d}y\, \frac{\delta F[G]}{\delta G[\phi(y)]}\frac{\delta G[\phi(y)]}{\delta\phi(x)} \tag{37}$$

- Specially:

$$\frac{\delta\phi(x)}{\delta\phi(y)} = \delta(x-y) \tag{38}$$

Functional calculus

- Consider

$$G[\phi(x)] \equiv \int \mathrm{d}x\, f(\phi(x), \phi'(x)) \tag{39}$$

where $\phi'(x) \equiv \frac{\mathrm{d}\phi}{\mathrm{d}x}$. We have

$$\begin{aligned}
\frac{\delta G[\phi]}{\delta \phi(x)} &= \lim_{h\to 0}\left[\int \mathrm{d}u\, f(\phi(u) + h\delta(x-u), \phi'(u) + h\delta'(x-u)) - \int \mathrm{d}u\, f(\phi(u), \phi'(u))\right] \\
&= \int \mathrm{d}u \left[\frac{\partial f(\phi,\phi')}{\partial \phi(u)}\delta(x-u) + \frac{\partial f(\phi,\phi')}{\partial \phi'(u)}\frac{\mathrm{d}}{\mathrm{d}u}\delta(x-u)\right] \\
&= \frac{\partial f(\phi,\phi')}{\partial \phi(x)} - \frac{\mathrm{d}}{\mathrm{d}x}\frac{\partial f(\phi,\phi')}{\partial \phi'(x)}
\end{aligned} \tag{40}$$

Born–Oppenheimer approximation

- BO approximation is in principle an adiabatic approximation, separating the nuclear and electron degrees of freedom in a molecule system.
- Molecule Hamiltonian:

$$\hat{H}_{\mathrm{M}} = \hat{T}_{\mathrm{N}} + \hat{V}_{\mathrm{N}} + \hat{T}_e + \hat{V}_e + \hat{V}_{e\mathrm{N}} \tag{41}$$

with nuclear coordinates $\{\boldsymbol{R}_a\} \equiv \underline{\boldsymbol{R}}$ and electron coordinates $\{\boldsymbol{r}_\alpha\}$.

- Electron Hamiltonian and electronic basis:

$$\hat{H}_{\mathrm{e}}(\{\hat{\boldsymbol{p}}_\alpha\}, \{\hat{\boldsymbol{r}}_\alpha\}; \underline{\boldsymbol{R}}) = \hat{T}_e(\{\hat{\boldsymbol{p}}_\alpha\}) + \hat{V}_e(\{\hat{\boldsymbol{r}}_\alpha\}) + \hat{V}_{e\mathrm{N}}(\{\hat{\boldsymbol{r}}_\alpha\}; \underline{\boldsymbol{R}}) \tag{42}$$

and

$$\hat{H}_e(\underline{\boldsymbol{R}})|\varphi_n(\underline{\boldsymbol{R}})\rangle = E_n(\underline{\boldsymbol{R}})|\varphi_n(\underline{\boldsymbol{R}})\rangle \tag{43}$$

- Expand the total wave function as

$$|\Psi(t; \underline{\boldsymbol{R}})\rangle \equiv \langle \underline{\boldsymbol{R}}|\Psi(t)\rangle = \sum_n \Xi_n(t; \underline{\boldsymbol{R}})|\varphi_n(\underline{\boldsymbol{R}})\rangle \tag{44}$$

Born–Oppenheimer approximation (**important**)

- Equation of motion for $\Xi_n(t;\underline{\boldsymbol{R}})$:

$$i\frac{\partial}{\partial t}\Xi_n = \sum_a \frac{1}{2M_a}(-i\nabla_a - \boldsymbol{A}_n^a)^2\Xi_n + U_n\Xi_n + \sum_{m\neq n}\Theta_{nm}\Xi_m \tag{45}$$

- Berry connection:

$$\boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) \equiv i\langle\varphi_n(\underline{\boldsymbol{R}})|\nabla_a|\varphi_n(\underline{\boldsymbol{R}})\rangle \tag{46}$$

- Adiabatic potential energy surface:

$$U_n \equiv E_n + V_{\mathrm{N}} + \sum_a \frac{1}{2M_a}\Big[(\boldsymbol{A}_n^a)^2 + (\nabla_a\langle\varphi_n|)\cdot(\nabla_a|\varphi_n\rangle)\Big] \tag{47}$$

- Nondiagonal coupling:

$$\Theta_{mn} \equiv -\sum_a \frac{1}{2M_a}\Big(2\langle\varphi_m|\nabla_a|\varphi_n\rangle\cdot\nabla_a + \langle\varphi_m|\nabla_a^2|\varphi_n\rangle\Big) \tag{48}$$

- BO approximation: $\Theta_{mn}\to 0(m\neq n)$, since

$$\frac{i\langle\varphi_m|\nabla_a|\varphi_n\rangle}{2M_a} = \frac{1}{2M_a}\frac{\langle\varphi_m(\underline{\boldsymbol{R}})|\nabla_a V_{\mathrm{eN}}|\varphi_n(\underline{\boldsymbol{R}})\rangle}{E_m(\underline{\boldsymbol{R}}) - E_n(\underline{\boldsymbol{R}})} \tag{49}$$

Geometric phase

- Consider a many degrees of freedom case. Define the Berry connection

$$\boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) \equiv i\langle\varphi_n(\underline{\boldsymbol{R}})|\nabla_a|\varphi_n(\underline{\boldsymbol{R}})\rangle \tag{50}$$

by defining $\underline{\boldsymbol{R}} \equiv \{\boldsymbol{R}_a\}$. Since the eigenstate would stay invariance under local gauge transformation

$$|\varphi_n(\underline{\boldsymbol{R}})\rangle \to e^{i\theta(\underline{\boldsymbol{R}})}|\varphi_n(\underline{\boldsymbol{R}})\rangle \tag{51}$$

The Berry connection goes as

$$\boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) \to \widetilde{\boldsymbol{A}}_n^a(\underline{\boldsymbol{R}}) = \boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) - \nabla_a\theta(\underline{\boldsymbol{R}}) \tag{52}$$

Therefore, if one can find a certain gauge such that

$$\boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) - \nabla_a\theta(\underline{\boldsymbol{R}}) = 0 \tag{53}$$

the integral

$$\gamma_n^a \equiv \oint_C \boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) \cdot \mathrm{d}\boldsymbol{R}_a = 0 \tag{54}$$

In the new gauge, the Berry connection vanishes.

Geometric phase

- Consider the integral

$$\gamma_n^a \equiv \oint_C \boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) \cdot \mathrm{d}\boldsymbol{R}_a = \iint_\Sigma \boldsymbol{\Omega}_n^a(\underline{\boldsymbol{R}}) \cdot \mathrm{d}\boldsymbol{\sigma}_a \tag{55}$$

with the Berry curvature defined as

$$\boldsymbol{\Omega}_n^a(\underline{\boldsymbol{R}}) \equiv \nabla_a \times \boldsymbol{A}_n^a(\underline{\boldsymbol{R}}) \tag{56}$$

- Berry curvature:

$$\boldsymbol{\Omega}_n^a(\underline{\boldsymbol{R}}) = i \sum_{m \neq n} \frac{\langle \varphi_m(\underline{\boldsymbol{R}}) | \nabla_a V_{12} | \varphi_n(\underline{\boldsymbol{R}}) \rangle \times \langle \varphi_n(\underline{\boldsymbol{R}}) | \nabla_a V_{12} | \varphi_m(\underline{\boldsymbol{R}}) \rangle}{[E_m(\underline{\boldsymbol{R}}) - E_n(\underline{\boldsymbol{R}})]^2} \tag{57}$$

- Degeneracy points meet singular points which leads to the AB effect.

Second quantization

- Consider a many-fermion Hamiltonian,

$$\hat{H} = \sum_{\alpha=1}^{N} \left[\frac{\hat{\boldsymbol{p}}_\alpha^2}{2m} + v(\hat{\boldsymbol{r}}_\alpha) \right] + \frac{1}{2} \sum_{\alpha \neq \beta} v(\hat{\boldsymbol{r}}_\alpha - \hat{\boldsymbol{r}}_\beta) \equiv \sum_\alpha \hat{h}_\alpha + \frac{1}{2} \sum_{\alpha \neq \beta} \hat{v}_{\alpha\beta} \tag{58}$$

- Given a set of single particle basis $\{|k\rangle\}$, define the antisymmetric basis

$$|k_1 k_2 \cdots k_N\rangle \equiv \frac{1}{\sqrt{N!}} \sum_P (-1)^p \mathcal{P}\Big(|k_1\rangle_1 \otimes |k_2\rangle_2 \otimes \cdots \otimes |k_N\rangle_N\Big) \tag{59}$$

  which is called the Slater determinant. Here $\mathcal{P}$ means the permutation of state $|k_\alpha\rangle$ with particle β and p is the parity of the permutation.

- Use the occupation numbers $\{n_i\}$ to label the state: $|n_1 n_2 \cdots\rangle \equiv |k_1 k_2 \cdots k_N\rangle$. For fermion, $n_i = 0, 1$.
- The orthonormality and completeness relations are

$$\langle n_1 n_2 \cdots | n_1' n_2' \cdots \rangle = \delta_{n_1 n_1'} \delta_{n_2 n_2'} \cdots \tag{60}$$

$$\sum_{n_1 n_2 \cdots} |n_1 n_2 \cdots\rangle\langle n_1 n_2 \cdots| = 1 \tag{61}$$

Second quantization

- Define the creation operators $\hat{a}_i^\dagger$ via

$$|k_1 k_2 \cdots k_N\rangle \equiv \hat{a}_{k_1}^\dagger \hat{a}_{k_2}^\dagger \cdots \hat{a}_{k_N}^\dagger |0\rangle \tag{62}$$

- Then it is easy to prove (**important**)

$$\{\hat{a}_i, \hat{a}_j^\dagger\} = \delta_{ij}, \ \{\hat{a}_i, \hat{a}_j\} = \{\hat{a}_i^\dagger, \hat{a}_j^\dagger\} = 0 \tag{63}$$

- For the occupation number representation,

$$\hat{a}_i^\dagger |n_1 n_2 \cdots n_i \cdots\rangle = (1 - n_i)(-)^{\sum_{j<i} n_j} |\cdots n_i + 1 \cdots\rangle \tag{64}$$

$$\hat{a}_i |n_1 n_2 \cdots n_i \cdots\rangle = n_i (-)^{\sum_{j<i} n_j} |\cdots n_i - 1 \cdots\rangle \tag{65}$$

Second quantization (**important**)

- It is shown that

$$\sum_\alpha |i\rangle_{\alpha\,\alpha}\langle j| = \hat{a}_i^\dagger \hat{a}_j \tag{66}$$

- For single particle operators,

$$\sum_\alpha \hat{h}_\alpha = \sum_{ij}\sum_\alpha {}_\alpha\langle i|\hat{h}_\alpha|j\rangle_\alpha \hat{a}_i^\dagger \hat{a}_j = \sum_{ij} h_{ij}\hat{a}_i^\dagger \hat{a}_j \tag{67}$$

with

$$h_{ij} \equiv \langle i|\hat{h}|j\rangle \tag{68}$$

- For two-body operators,

$$\frac{1}{2}\sum_{\alpha\neq\beta} \hat{v}_{\alpha\beta} = \frac{1}{2}\sum_{ijk\ell} v_{ijk\ell}\hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_\ell \hat{a}_k \tag{69}$$

with

$$v_{ijk\ell} \equiv {}_1\langle i|{}_2\langle j|\hat{v}_{12}|k\rangle_1|\ell\rangle_2 \tag{70}$$

Second quantization (**important**)

- Given two sets of single particle states $\{|i\rangle\}$ and $\{|\lambda\rangle\}$, we have

$$|\lambda\rangle = \sum_i |i\rangle\langle i|\lambda\rangle \tag{71}$$

  Then

$$\hat{b}_\lambda^\dagger = \sum_i \langle i|\lambda\rangle \hat{a}_i^\dagger \tag{72}$$

- For the spin–orbit representation, $|i\rangle \to |i\sigma\rangle$,

$$\hat{\psi}_\sigma(\boldsymbol{r}) = \sum_i \langle \boldsymbol{r}|i\rangle \hat{a}_{i\sigma} \equiv \sum_i \varphi_i(\boldsymbol{r})\hat{a}_{i\sigma} \tag{73}$$

  This is called the field operator, satisfying

$$\{\hat{\psi}_\sigma(\boldsymbol{r}), \hat{\psi}_{\sigma'}^\dagger(\boldsymbol{r}')\} = \delta_{\sigma\sigma'}\delta(\boldsymbol{r}-\boldsymbol{r}'),\ \{\hat{\psi}_\sigma(\boldsymbol{r}), \hat{\psi}_{\sigma'}(\boldsymbol{r}')\} = \{\hat{\psi}_\sigma^\dagger(\boldsymbol{r}), \hat{\psi}_{\sigma'}^\dagger(\boldsymbol{r}')\} = 0 \tag{74}$$

  The particle density operator is given by

$$\hat{n}(\boldsymbol{r}) \equiv \sum_{\sigma=\uparrow,\downarrow} \hat{\psi}_\sigma^\dagger(\boldsymbol{r})\hat{\psi}_\sigma(\boldsymbol{r}) \tag{75}$$

Second quantization

- Example: Define the particle density operator as

$$\hat{n}(\boldsymbol{r}) \equiv \sum_{\alpha} \delta(\boldsymbol{r} - \hat{\boldsymbol{r}}_{\alpha}) \tag{76}$$

The second quantization form reads

$$\begin{aligned} \hat{n}(\boldsymbol{r}) &= \sum_{\sigma} \sum_{ij} \hat{a}^{\dagger}_{i\sigma} \hat{a}_{j\sigma} \int \mathrm{d}\boldsymbol{r}' \, \varphi_i^*(\boldsymbol{r}') \delta(\boldsymbol{r} - \boldsymbol{r}') \varphi_j(\boldsymbol{r}') \\ &= \sum_{\sigma} \sum_{ij} \hat{a}^{\dagger}_{i\sigma} \hat{a}_{j\sigma} \varphi_i^*(\boldsymbol{r}) \varphi_j(\boldsymbol{r}) \\ &= \sum_{\sigma=\uparrow,\downarrow} \hat{\psi}^{\dagger}_{\sigma}(\boldsymbol{r}) \hat{\psi}_{\sigma}(\boldsymbol{r}) \end{aligned} \tag{77}$$

- Exercise: Show that

$$\hat{\gamma}(\boldsymbol{r}_1, \boldsymbol{r}_2) \equiv \sum_{\alpha \neq \beta} \delta(\boldsymbol{r}_1 - \hat{\boldsymbol{r}}_{\alpha}) \delta(\boldsymbol{r}_2 - \hat{\boldsymbol{r}}_{\beta}) = \sum_{\sigma_1, \sigma_2} \hat{\psi}^{\dagger}_{\sigma_1}(\boldsymbol{r}_1) \hat{\psi}^{\dagger}_{\sigma_2}(\boldsymbol{r}_2) \hat{\psi}_{\sigma_2}(\boldsymbol{r}_2) \hat{\psi}_{\sigma_1}(\boldsymbol{r}_1) \tag{78}$$

Quantum chemistry in second quantization

- Spin-orbit wave function as basis: $\chi_j(\boldsymbol{x}) \equiv \chi_j(\boldsymbol{r}, s) \equiv \varphi_j(\boldsymbol{r})\sigma(s) \equiv \langle \boldsymbol{r} s | j\sigma \rangle$
- Creation operator:

$$\hat{a}^{\dagger}_{j\sigma} |0\rangle \equiv |j\sigma\rangle \tag{79}$$

- Electron Hamiltonian:

$$\hat{H} = \sum_{\alpha=1}^{N} \left[\frac{\hat{\boldsymbol{p}}_{\alpha}^2}{2} + v(\hat{\boldsymbol{r}}_{\alpha}) \right] + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{1}{|\hat{\boldsymbol{r}}_{\alpha} - \hat{\boldsymbol{r}}_{\beta}|} \tag{80}$$

- Kinetics part:

$$\hat{T} = \sum_{\alpha} \frac{\hat{\boldsymbol{p}}_{\alpha}^2}{2} = \sum_{ij} \sum_{\sigma} t_{ij} \hat{a}^{\dagger}_{i\sigma} \hat{a}_{j\sigma} \tag{81}$$

with

$$t_{ij} \equiv -\frac{1}{2} \int \mathrm{d}\boldsymbol{r}\, \varphi_i^*(\boldsymbol{r}) \nabla^2 \varphi_j(\boldsymbol{r}) \tag{82}$$

Quantum chemistry in second quantization

- External potential:

$$\sum_{\alpha} \hat{v}(\hat{\boldsymbol{r}}_\alpha) = \sum_{ij} \sum_{\sigma} v_{ij} \hat{a}^\dagger_{i\sigma} \hat{a}_{j\sigma} \tag{83}$$

with

$$v_{ij} \equiv \int \mathrm{d}\boldsymbol{r}\, \varphi_i^*(\boldsymbol{r}) v(\boldsymbol{r}) \varphi_j(\boldsymbol{r}) \tag{84}$$

- Coulomb interaction:

$$\frac{1}{2} \sum_{\alpha \neq \beta} \frac{1}{|\hat{\boldsymbol{r}}_\alpha - \hat{\boldsymbol{r}}_\beta|} = \frac{1}{2} \sum_{ijk\ell} \sum_{\sigma\sigma'} \langle ij||kl\rangle \hat{a}^\dagger_{i\sigma} \hat{a}^\dagger_{j\sigma'} \hat{a}_{\ell\sigma'} \hat{a}_{k\sigma} \tag{85}$$

with

$$\langle ij||k\ell\rangle \equiv \iint \mathrm{d}\boldsymbol{r}_1 \mathrm{d}\boldsymbol{r}_2 \frac{\varphi_i^*(\boldsymbol{r}_1)\varphi_j^*(\boldsymbol{r}_2)\varphi_k(\boldsymbol{r}_1)\varphi_\ell(\boldsymbol{r}_2)}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \tag{86}$$

Homework1206-2

- Hamiltonian:

$$\hat{H} = \sum_{\alpha=1}^{N} \left[\frac{\hat{p}_\alpha^2}{2m} + V_0 \delta(\hat{x}_\alpha) \right] \tag{87}$$

- Single particle state: $|k\sigma\rangle$, satisfying $\hat{p}|k\sigma\rangle = \hbar k|k\sigma\rangle$ and $\hat{S}|k\sigma\rangle = \frac{\hbar\sigma}{2}|k\sigma\rangle$. Here $k = \frac{2\pi n}{L}$ $(n = 0, \pm 1, \pm 2, \cdots)$ and L is the length of the box.
- Kinetics part:

$$\sum_\alpha \frac{\hat{p}_\alpha^2}{2m} = \sum_{kk'} \sum_{\sigma\sigma'} \hat{a}^\dagger_{k\sigma} \hat{a}_{k'\sigma'} \langle k\sigma| \frac{\hat{p}^2}{2m} |k'\sigma'\rangle = \sum_{k\sigma} \frac{\hbar^2 k^2}{2m} \hat{a}^\dagger_{k\sigma} \hat{a}_{k\sigma} \tag{88}$$

- External potential:

$$\sum_\alpha V_0 \delta(\hat{x}_\alpha) = \sum_{kk'} \sum_{\sigma\sigma'} \hat{a}^\dagger_{k\sigma} \hat{a}_{k'\sigma'} \langle k\sigma| V_0 \delta(\hat{x}) |k'\sigma'\rangle = \sum_{kk'} \sum_{\sigma} \frac{V_0}{L} \hat{a}^\dagger_{k\sigma} \hat{a}_{k'\sigma} \tag{89}$$

by using

$$\langle k\sigma| V_0 \delta(\hat{x}) |k'\sigma'\rangle = \delta_{\sigma\sigma'} \frac{V_0}{L} \int_{-L/2}^{L/2} \mathrm{d}x \, e^{-i(k-k')x} \delta(x) = \frac{V_0}{L} \delta_{\sigma\sigma'} \tag{90}$$

Homework1206-2

- Treat V_0 as a small quantity. The ground state of kinetics part is

$$|G\rangle = \prod_{|k|\leq k_F} \prod_{\sigma} \hat{a}^{\dagger}_{k\sigma}|0\rangle \tag{91}$$

with $k_F = \frac{2\pi n_F}{L}$ being the maximum value of k. Suppose N is even, it satisfies

$$N = \sum_k \sum_\sigma \langle G|\hat{a}^{\dagger}_{k\sigma}\hat{a}_{k\sigma}|G\rangle = 2\sum_{|k|\leq k_F} 1 = 2(2n_F + 1) \tag{92}$$

The ground state energy of kinetics part is

$$\begin{aligned} E^{(0)} &= \langle G|\sum_{k\sigma} \frac{\hbar^2 k^2}{2m}\hat{a}^{\dagger}_{k\sigma}\hat{a}_{k\sigma}|G\rangle = \frac{\hbar^2}{2m}\sum_{k\sigma} k^2\theta(k - k_F) \\ &= \frac{\hbar^2(2\pi)^2}{2mL^2} \times 2\sum_{|n|<n_F} n^2 \end{aligned} \tag{93}$$

- First order correction:

$$E^{(1)} = \langle G|\sum_{kk'}\sum_{\sigma} \frac{V_0}{L}\hat{a}^{\dagger}_{k\sigma}\hat{a}_{k'\sigma}|G\rangle = \frac{V_0}{L}\sum_{k\sigma}\langle G|\hat{a}^{\dagger}_{k\sigma}\hat{a}_{k\sigma}|G\rangle = \frac{V_0}{L}N \tag{94}$$

Quantum field theory

- Dirac equation cannot be a correct relativistic quantum theory since the Einstein relation $E = mc^2$ holds. The identity suggests the number of particles is not conserved when energy is large enough.
- As $E > m_e c^2$, the electron will suffer high energy reactions, such as

$$\gamma + \gamma \longrightarrow \mathrm{e}^+ + \mathrm{e}^- \tag{95}$$

- Second quantization form is not limited by the particle number, i.e.,

$$\sum_{\alpha=1}^{N} \hat{h}(i) \longrightarrow \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j \text{ (does not depend on } N) \tag{96}$$

- Actually, $\hat{a}_i/\hat{a}_i^\dagger$ connects different particle number subspaces, that is,

$$\hat{a}_i/\hat{a}_i^\dagger : \mathcal{H}_N \to \mathcal{H}_{N\mp 1} \tag{97}$$

- This makes us possible to generalize the quantum theory to the quantum field theory.
- Core problem of solving a many–body system: Evaluate

$$\langle \Omega | \hat{\psi}_1^\pm(x_1) \cdots \hat{\psi}_N^\pm(x_N) | \Omega \rangle \tag{98}$$

Group theory

- Definition: Group $\mathbb{G}$ is a set composed of $\{a, b, \cdots\}$, with multiplication operation $\cdot$ satisfying:
  - closure: $\forall a, b \in \mathbb{G}$, $a \cdot b \in \mathbb{G}$;
  - associativity: $\forall a, b, c \in \mathbb{G}$, $(a \cdot b) \cdot c = a \cdot (b \cdot c)$;
  - identity element: $\forall g \in G$, $\exists e \in \mathbb{G}$, $e \cdot g = g \cdot e = e$;
  - inverse element: $\forall g \in \mathbb{G}$, $\exists g^{-1} \in \mathbb{G}$, $g \cdot g^{-1} = g^{-1} \cdot g = e$, and g^{-1} is unique.

  We always omit $\cdot$, i.e., $a \cdot b \equiv ab$.

Representation of a group

- Consider a set of vectors $\{|\psi_n\rangle\}$ belong to a linear space $\mathbb{L}$.
- The group elements are operations on $\{|\psi_n\rangle\}$, i.e.,

$$g \to \hat{g}, \quad \hat{g}|\psi_n\rangle = \sum_m \Lambda_{mn}(g)|\psi_m\rangle \tag{99}$$

where

$$\Lambda_{mn}(g) \equiv \langle\psi_m|\hat{g}|\psi_n\rangle \equiv [\mathbf{\Lambda}(g)]_{mn} \tag{100}$$

is a matrix representation of $\hat{g}$. It satisfies

$$\mathbf{\Lambda}(gh) = \mathbf{\Lambda}(g)\mathbf{\Lambda}(h) \tag{101}$$

The dimension of $\mathbb{L}$ is called the dimension of representation.

- Specially, for $\dim\mathbb{L} = 1$, $\mathbf{\Lambda}(g) = 1$, called the unit representation.
- If the map $g \to \mathbf{\Lambda}(g)$ is one-to-one, it is called the faithful representation.

Reducible vs. irreducible representation

- For a set of basis function $\{|\psi_n\rangle\}_{n=1}^{N}$, we separate them into several subsets with elements numbers, $N_1 + N_2 + \cdots = N$. For one of those subsets, e.g., $\{|\psi_n\rangle\}_{n=1}^{N_1}$, if

$$\hat{g}|\psi_n\rangle \in \{|\psi_n\rangle\}_{n=1}^{N_1} \quad \forall g \in \mathbb{G} \tag{102}$$

  we say $\{|\psi_n\rangle\}_{n=1}^{N_1}$ is a reducible representation of $\mathbb{G}$.
- If N_1 is the smallest choice, we say $\{|\psi_n\rangle\}_{n=1}^{N_1}$ is an irreducible representation of $\mathbb{G}$.
- Any reducible representation can be decomposed into several irreducible representations.
- That is to say, all matrices $\{\Lambda(g)|g \in \mathbb{G}\}$ cannot be block diagonalized simultaneously. For example,

$$\Lambda(g) \sim \sum_k \oplus \Lambda^k(g) \sim \begin{pmatrix} \Lambda^1(g) & 0 & \cdots & 0 \\ 0 & \Lambda^2(g) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \Lambda^K(g) \end{pmatrix} \tag{103}$$

Great orthogonality theorem

- The great orthogonality theorem

$$(\Lambda^{k'}_{m'n'}|\Lambda^{k}_{mn}) \equiv \frac{1}{h}\sum_{g}\Lambda^{k}_{mn}(g)[\Lambda^{k'}_{m'n'}(g)]^{*} = \frac{1}{\ell_k}\delta_{kk'}\delta_{mm'}\delta_{nn'} \tag{104}$$

The size of $\mathbb{G}$ is h and ℓ_k is the dimension of k-th irreducible representation.

- Character: $\chi(g) \equiv \mathrm{Tr}\boldsymbol{\Lambda}(g)$. Thus

$$\frac{1}{h}\sum_{g}\chi^{k}(g)[\chi^{k'}(g)]^{*} = \frac{1}{\ell_k}\sum_{mn}\delta_{kk'}\delta_{mn} = \delta_{kk'} \tag{105}$$

- Burnside's theorem:

$$h = \ell_1^2 + \ell_2^2 + \cdots + \ell_K^2 \tag{106}$$

Character table

- Conjugacy class of $g \in \mathbb{G}$: $\mathbb{K}(g) \equiv \{hgh^{-1} | h \in \mathbb{G}\}$.
- $\{\mathbb{K}_\alpha\}$ are all the conjugacy classes of $\mathbb{G}$. Then $\mathbb{G} = \bigcup_\alpha \mathbb{K}_\alpha$ and $\mathbb{K}_\alpha \bigcap \mathbb{K}_{\alpha'} = 0$ $(\alpha \neq \alpha')$.
- $\chi(g) = \chi(hgh^{-1})$: Conjugacy class shares the same character.
- Orthogonality:

$$\sum_\alpha h_\alpha \chi^k(\mathbb{K}_\alpha)[\chi^{k'}(\mathbb{K}_\alpha)]^* = h\delta_{kk'}, \tag{107}$$

$$\sum_k \chi^k(\mathbb{K}_\alpha)[\chi^k(\mathbb{K}_{\alpha'})]^* = \frac{h}{h_\alpha}\delta_{\alpha\alpha'} \tag{108}$$

with h_k being the number of elements in K_α.

- Character table:

	$\mathbb{K}_1 \equiv \{e\}$	$\mathbb{K}_2$	$\cdots$	$\mathbb{K}_K$
Λ_1	1	1	$\cdots$	1
Λ_2	$\chi^2(\mathbb{K}_1)$	$\chi^2(\mathbb{K}_2)$	$\cdots$	$\chi^2(\mathbb{K}_K)$
$\vdots$	$\vdots$	$\vdots$	$\ddots$	$\vdots$
Λ_K	$\chi^K(\mathbb{K}_1)$	$\chi^K(\mathbb{K}_2)$	$\cdots$	$\chi^K(\mathbb{K}_K)$

More on Born–Oppenheimer approximation

- BO approximation is in principle an adiabatic approximation, which separates the slow and fast variables of a Hamiltonian.
- Consider a system with Hamiltonian:

$$\hat{H} = \hat{H}_1(\hat{p}, \hat{q}) + \hat{H}_2(\hat{P}, \hat{Q}) + \hat{V}_{12}(\hat{q}, \hat{Q}) \tag{109}$$

- q: fast; Q: slow.
- In the $\hat{H}_2$-interaction picture:

$$e^{-i\hat{H}(t-t_0)}|\Psi(t_0)\rangle = e^{-i\hat{H}_2(t-t_0)}\hat{U}_I(t,t_0)|\Psi(t_0)\rangle \equiv e^{-i\hat{H}_2(t-t_0)}|\Psi(t)\rangle_I \tag{110}$$

and

$$i\frac{\partial}{\partial t}\hat{U}_I(t,t_0) = \left[\hat{H}_1(\hat{p},\hat{q}) + \hat{V}_{12}(\hat{q},\hat{Q}(t))\right]\hat{U}_I(t,t_0) \equiv \hat{H}_I(\hat{Q}(t))\hat{U}_I(t,t_0) \tag{111}$$

with $\hat{Q}(t) \equiv e^{i\hat{H}_2(t-t_0)}\hat{Q}e^{-i\hat{H}_2(t-t_0)}$.

Adiabatic approximation

- In the interaction picture, the slow variable behaves like an external field but is slowly varying with t.
- Construct the simultaneous basis:

$$\hat{H}_I(\hat{Q}_1)|\varphi_n(\hat{Q}_1)\rangle = E_n(\hat{Q}_1)|\varphi_n(\hat{Q}_1)\rangle \tag{112}$$

and a unitary operator

$$\hat{U}(\hat{Q}_1, \hat{Q}_0) \equiv \sum_n |\varphi_n(\hat{Q}_1)\rangle\langle\varphi_n(\hat{Q}_0)| \tag{113}$$

such that $\hat{U}(\hat{Q}_1, \hat{Q}_0)|\varphi_n(\hat{Q}_0)\rangle = |\varphi_n(\hat{Q}_1)\rangle$.

- Transform the Hamiltonian $\hat{H}_I(Q)$ as

$$\widetilde{H}_I(\hat{Q}(t)) \equiv \hat{U}^\dagger(\hat{Q}(t), \hat{Q}(t_0))\hat{H}_I(\hat{Q}(t))\hat{U}(\hat{Q}(t), \hat{Q}(t_0)) \tag{114}$$

This leads to

$$\widetilde{H}_I(\hat{Q}(t))|\varphi_n(\hat{Q}(t_0))\rangle = E_n(\hat{Q}(t))|\varphi_n(\hat{Q}(t_0))\rangle \tag{115}$$

Adiabatic approximation

- The completeness relation of the simultaneous basis reads

$$\sum_n |\varphi_n(\hat{Q}_1)\rangle\langle\varphi_n(\hat{Q}_1)| = \sum_n \int \mathrm{d}Q\, |\varphi_n(Q)\rangle|Q\rangle\langle Q|\langle\varphi_n(Q)| = 1 \tag{116}$$

- More rigorously,

$$\begin{aligned}
&\hat{U}(\hat{Q}(t), \hat{Q}(t_0)) \\
&= \sum_n |\varphi_n(\hat{Q}(t))\rangle\langle\varphi_n(\hat{Q}(t_0))| \\
&= \sum_n e^{i\hat{H}_2(t-t_0)}|\varphi_n(\hat{Q})\rangle e^{-i\hat{H}_2(t-t_0)}\langle\varphi_n(\hat{Q})| \\
&= \sum_n \iint \mathrm{d}Q\mathrm{d}Q' e^{i\hat{H}_2(t-t_0)}|\varphi_n(Q)\rangle|Q\rangle\langle Q|e^{-i\hat{H}_2(t-t_0)}|Q'\rangle\langle Q'|\langle\varphi_n(Q')|
\end{aligned} \tag{117}$$

Adiabatic approximation

- For the Schrödinger equation,

$$i\frac{\mathrm{d}}{\mathrm{d}t}|\Psi(t)\rangle_I = \hat{H}_I(\hat{Q}(t))|\Psi(t)\rangle_I \tag{118}$$

by defining $|\widetilde{\Psi}(t)\rangle_I \equiv \hat{U}^\dagger(\hat{Q}(t))|\Psi(t)\rangle_I$ with $\hat{U}(\hat{Q}(t)) \equiv \hat{U}(\hat{Q}(t), \hat{Q}(t_0))$, we have

$$i\frac{\mathrm{d}}{\mathrm{d}t}|\widetilde{\Psi}(t)\rangle_I = \left[\widetilde{H}(\hat{Q}(t)) + \hat{\Delta}(\hat{Q}(t))\right]|\widetilde{\Psi}(t)\rangle_I \tag{119}$$

with

$$\hat{\Delta}(\hat{Q}(t)) \equiv i\left[\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}(\hat{Q}(t))\right]^\dagger \hat{U}(\hat{Q}(t)) = -i\hat{U}^\dagger(\hat{Q}(t))\frac{\mathrm{d}}{\mathrm{d}t}\hat{U}(\hat{Q}(t)) \tag{120}$$

- In the $|\varphi_n(\hat{Q})\rangle$ representation, we have

$$\widetilde{H}_{mn}(\hat{Q}(t)) = \delta_{mn}E_n(\hat{Q}(t)) \tag{121}$$

and

$$\Delta_{mn}(\hat{Q}(t)) = -i\langle\varphi_m(\hat{Q}(t))|\frac{\mathrm{d}}{\mathrm{d}t}|\varphi_n(\hat{Q}(t))\rangle \tag{122}$$

Adiabatic approximation

- Consider

$$\hat{H}_I(t)|\varphi_n(t)\rangle = E_n(t)|\varphi_n(t)\rangle \tag{123}$$

and we have for $m \neq n$

$$\langle\varphi_m(t)|\frac{\mathrm{d}}{\mathrm{d}t}\hat{H}_I(t)|\varphi_n(t)\rangle = -\big[E_m(t) - E_n(t)\big]\langle\varphi_m(t)|\frac{\mathrm{d}}{\mathrm{d}t}|\varphi_n(t)\rangle \tag{124}$$

- The off–diagonal elements of $\Delta_{mn}(t)$ are given by

$$|\Delta_{mn}(t)| = \left|\langle\varphi_m(t)|\frac{\mathrm{d}}{\mathrm{d}t}|\varphi_n(t)\rangle\right| = \left|\frac{\langle\varphi_m(t)|\frac{\mathrm{d}}{\mathrm{d}t}\hat{H}_I(t)|\varphi_n(t)\rangle}{E_m(t) - E_n(t)}\right| \ll 1 \tag{125}$$

- The adiabatic approximation reads

$$\Delta_{mn}(t) \to \Delta_{nn}(t)\delta_{mn} \tag{126}$$

- The solution of Eq. (119) is then given by

$$|\widetilde{\Psi}(t)\rangle_I = \sum_n |\varphi_n(\hat{Q})\rangle\hat{\Lambda}(t,t_0)\langle\varphi_n(\hat{Q})|\widetilde{\Psi}(t_0)\rangle \tag{127}$$

with

$$\hat{\Lambda}(t,t_0) \equiv T_+ e^{-i\int_{t_0}^{t}\mathrm{d}\tau\,[E_n(\hat{Q}(\tau))+\Delta_{nn}(\hat{Q}(\tau))]} \tag{128}$$

Adiabatic approximation

- The final solution reads

$$|\Psi(t)\rangle_I = \sum_n |\varphi_n(\hat{Q}(t))\rangle T_+ e^{-i\int_{t_0}^{t} \mathrm{d}\tau\,[E_n(\hat{Q}(\tau))+\Delta_{nn}(\hat{Q}(\tau))]} \langle\varphi_n(\hat{Q})|\widetilde{\Psi}(t_0)\rangle \tag{129}$$

- Therefore, we have

$$\begin{aligned} &|\Psi(t)\rangle \\ =\ & e^{-i\hat{H}_2(t-t_0)}|\Psi(t)\rangle_I \\ =\ & \sum_n |\varphi_n(\hat{Q})\rangle e^{-i\hat{H}_2(t-t_0)} T_+ e^{-i\int_{t_0}^{t} \mathrm{d}\tau\,[E_n(\hat{Q}(\tau))+\Delta_{nn}(\hat{Q}(\tau))]} \langle\varphi_n(\hat{Q})|\Psi(t_0)\rangle \end{aligned} \tag{130}$$

- The derivative goes by

$$i\frac{\mathrm{d}}{\mathrm{d}t}\langle\varphi_n(\hat{Q})|\Psi(t)\rangle = \left[\hat{H}_2(\hat{P},\hat{Q}) + E_n(\hat{Q}) + \Delta_n(\hat{P},\hat{Q})\right]\langle\varphi_n(\hat{P},\hat{Q})|\Psi(t)\rangle \tag{131}$$

where

$$\Delta_n(\hat{P},\hat{Q}) = \langle\varphi_n(\hat{Q})|[\hat{H}_2, |\varphi_n(\hat{Q})\rangle] \tag{132}$$

BO approximation revisit

- Consider that

$$\hat{H}_2(\hat{P},\hat{Q}) = \frac{\hat{P}^2}{2M} + V(\hat{Q}) \tag{133}$$

Expand Eq. (131) into the Q-representation, that is,

$$i\frac{\partial}{\partial t}\Xi_n(t;Q) = \left[\hat{H}_2(-i\partial_Q, Q) + E_n(Q) + \Delta_n(-i\partial_Q, Q)\right]\Xi_n(t;Q) \tag{134}$$

where $\Xi_n(t;Q) \equiv \langle Q|\langle\varphi_n(Q)|\Psi(t)\rangle$ and $\partial_Q \equiv \frac{\partial}{\partial Q}$.

- Consider

$$\begin{aligned}
[\hat{H}_1, |\varphi_n(\hat{Q})\rangle] &= \frac{1}{2M}[\hat{P}^2, |\varphi_n(\hat{Q})\rangle] = \frac{1}{2M}\left(\hat{P}^2|\varphi_n(\hat{Q})\rangle - |\varphi_n(\hat{Q})\rangle\hat{P}^2\right) \\
&= \frac{1}{2M}\hat{P}[\hat{P}, |\varphi_n(\hat{Q})\rangle] + \frac{1}{2M}[\hat{P}, |\varphi_n(\hat{Q})\rangle]\hat{P} \\
&= \frac{-i}{2M}\left[\hat{P}\frac{\partial}{\partial\hat{Q}}|\varphi_n(\hat{Q})\rangle + \frac{\partial}{\partial\hat{Q}}|\varphi_n(\hat{Q})\rangle\hat{P}\right] \\
&= -\frac{i}{M}\frac{\partial}{\partial\hat{Q}}|\varphi_n(\hat{Q})\rangle\hat{P} - \frac{1}{2M}\frac{\partial^2}{\partial\hat{Q}^2}|\varphi_n(\hat{Q})\rangle
\end{aligned} \tag{135}$$

BO approximation revisit

- Therefore,

$$\Delta_n(\hat{P},\hat{Q}) = -\frac{i}{M}\langle\varphi_n(\hat{Q})|\frac{\partial}{\partial\hat{Q}}|\varphi_n(\hat{Q})\rangle\hat{P} - \frac{1}{2M}\langle\varphi_n(\hat{Q})|\frac{\partial^2}{\partial\hat{Q}^2}|\varphi_n(\hat{Q})\rangle \tag{136}$$

and in the Q-representation, it reads

$$\Delta_n = -\frac{1}{M}\langle\varphi_n(Q)|\frac{\partial}{\partial Q}|\varphi_n(Q)\rangle\frac{\partial}{\partial Q} - \frac{1}{2M}\langle\varphi_n(Q)|\frac{\partial^2}{\partial Q^2}|\varphi_n(Q)\rangle \tag{137}$$

and the kinetic part can be recast as

$$\frac{\hat{P}^2}{2M} \to \frac{1}{2M}\left[\hat{P} - i\langle\varphi_n(\hat{Q})|\frac{\partial}{\partial\hat{Q}}|\varphi_n(\hat{Q})\rangle\right]^2 \tag{138}$$

- The Hamiltonian corresponds to Ξ_n can be recast as (**important**)

$$\hat{H}_{\text{eff}} = \frac{1}{2M}\left[\hat{P} - i\langle\varphi_n(\hat{Q})|\frac{\partial}{\partial\hat{Q}}|\varphi_n(\hat{Q})\rangle\right]^2 + U(\hat{Q}) \tag{139}$$

with

$$U = E_n + V + \frac{1}{2M}\left[\frac{\partial}{\partial Q}\langle\varphi_n(Q)|\frac{\partial}{\partial Q}|\varphi_n(Q)\rangle + \left(\langle\varphi_n(Q)|\frac{\partial}{\partial Q}|\varphi_n(Q)\rangle\right)^2\right] \tag{140}$$