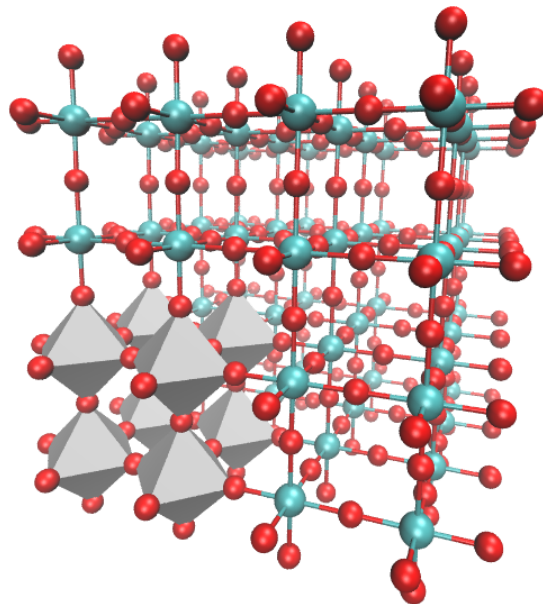




Techniques of Approximation

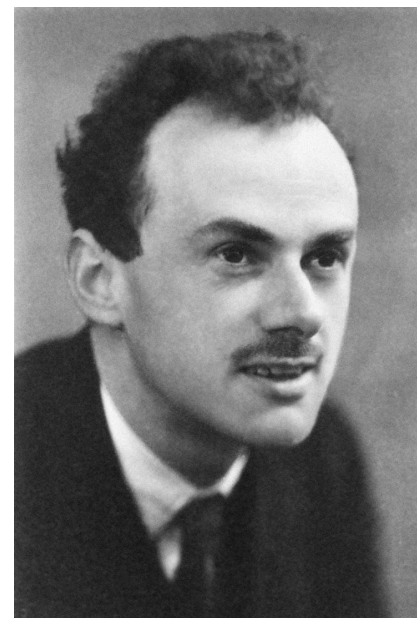


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Introduction

Beyond analytical solutions

- The underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble. It therefore becomes desirable that approximate practical methods of applying quantum mechanics should be developed, which can lead to an explanation of the main features of complex atomic systems without too much computation.
- Going beyond the two-body problem (almost everything of interest to chemists) has no analytic solution
- Methods of finding numerical solutions required
 - Perturbation theory
 - Variational principle



P. A. M. Dirac
1902-1984

Perturbation Theory

Time-independent perturbation theory

- Assume Hamiltonian of true system and a simpler (solvable) system differ by a time-independent contribution

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}$$

- $\hat{H}^{(1)}$ is the **perturbation** and $\hat{H}^{(0)}$ is the **unperturbed system**
- For example, perturbation could be a bump in the particle in a box potential
- The true energy of the system differs from the unperturbed system according to:

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \dots$$

First-order correction

Second-order correction

- Second-order correction is proportional to $(\hat{H}^{(1)})^2$
- The true wavefunction of the system differs from the unperturbed system according to:

$$\Psi = \Psi^{(0)} + \Psi^{(1)} + \Psi^{(2)} + \dots$$

- How can we compute these quantities?

Perturbation Theory

Two-level system

- First let's study system with only two eigenstates

$$\hat{H}^{(0)} |\Psi_1^{(0)}\rangle = E_1^{(0)} |\Psi_1^{(0)}\rangle$$

$$\hat{H}^{(0)} |\Psi_2^{(0)}\rangle = E_2^{(0)} |\Psi_2^{(0)}\rangle$$

- If the eigenstates of the solvable system form a complete set (generally true) then the eigenstates of the true system can be written as a linear combination

$$\hat{H} |\Psi\rangle = E |\Psi\rangle$$

$$|\Psi\rangle = c_1 |\Psi_1^{(0)}\rangle + c_2 |\Psi_2^{(0)}\rangle$$

- c_1 and c_2 are the coefficients to be determined

$$(\hat{H} - E) |\Psi\rangle \Rightarrow (\hat{H} - E)(c_1 |\Psi_1^{(0)}\rangle + c_2 |\Psi_2^{(0)}\rangle) \Rightarrow c_1(\hat{H} - E) |\Psi_1^{(0)}\rangle + c_2(\hat{H} - E) |\Psi_2^{(0)}\rangle = 0$$

$$\langle \Psi_1^{(0)} | c_1(\hat{H} - E) |\Psi_1^{(0)}\rangle + \langle \Psi_1^{(0)} | c_2(\hat{H} - E) |\Psi_2^{(0)}\rangle \Rightarrow c_1(H_{11} - E) + c_2 H_{12} = 0$$

$$\langle \Psi_2^{(0)} | c_1(\hat{H} - E) |\Psi_1^{(0)}\rangle + \langle \Psi_2^{(0)} | c_2(\hat{H} - E) |\Psi_2^{(0)}\rangle \Rightarrow c_1 H_{21} + c_2(H_{22} - E) = 0$$

- Where we have used orthonormality and introduced the definition of a matrix element

$$\langle \Psi_i^{(0)} | \hat{H} | \Psi_j^{(0)} \rangle = H_{ij} \qquad \langle \Psi_i^{(0)} | \Psi_j^{(0)} \rangle = \delta_{ij}$$

Perturbation Theory

Two-level system

- Solve the simultaneous equations using the determinant

$$\begin{aligned} c_1(H_{11} - E) + c_2H_{12} &= 0 \\ c_1H_{21} + c_2(H_{22} - E) &= 0 \end{aligned} \longrightarrow \begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

- Expanding out the determinant, the two-level perturbed system energies are

$$E^2 + (-H_{11} - H_{22})E + H_{11}H_{22} - H_{12}H_{21} = 0$$

$$E_{\pm} = \frac{1}{2}(H_{11} + H_{22}) \pm \frac{1}{2}\{(H_{11} - H_{22})^2 + 4H_{12}H_{21}\}^{1/2}$$

- Let's examine the consequences of our derivation
 - Assume that the unperturbed system and the perturbation have the form:

$$\mathbf{H} = \begin{bmatrix} E_1^{(0)} & 0 \\ 0 & E_2^{(0)} \end{bmatrix} + \begin{bmatrix} 0 & H_{12}^{(1)} \\ H_{12}^{(1)} & 0 \end{bmatrix}$$

$$E_{\pm} = \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) \pm \frac{1}{2}\{(E_1^{(0)} - E_2^{(0)})^2 + 4\epsilon^2\}^{1/2} \quad \epsilon^2 = H_{12}^{(1)2}$$

Perturbation Theory

Two-level system

$$E_{\pm} = \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) \pm \frac{1}{2}\{(E_1^{(0)} - E_2^{(0)})^2 + 4\varepsilon^2\}^{1/2}$$

- Limit $\varepsilon=0$:

$$E_{\pm} = \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) \pm \frac{1}{2}(E_1^{(0)} - E_2^{(0)})$$

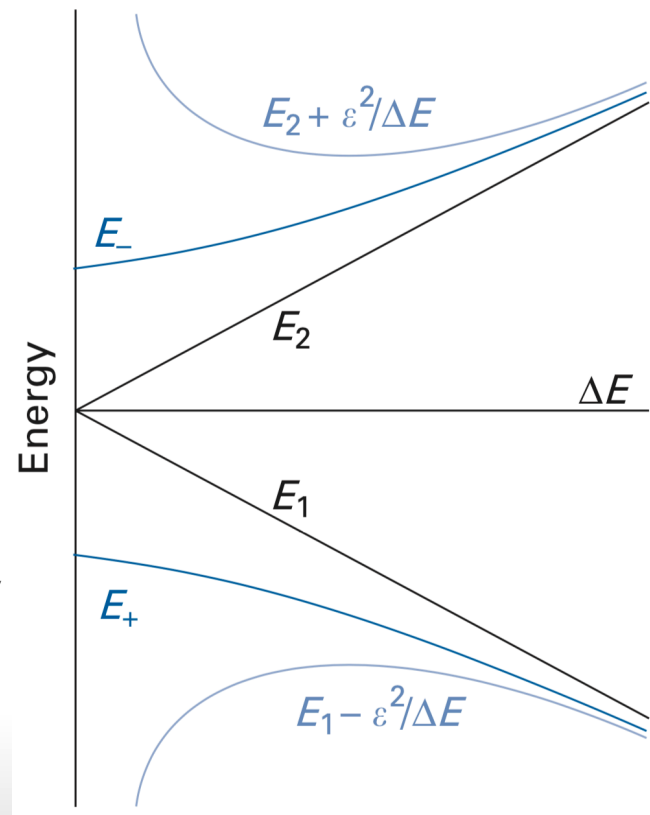
- Limit $E_1^{(0)}=E_2^{(0)}$:

$$E_{\pm} = E_1^{(0)} \pm \varepsilon \quad \Delta E_{\pm} = 2\varepsilon$$

- Expression for the energy correction to second order:

$$\sqrt{1+x} = 1 + \frac{1}{2}x + \frac{1}{8}x^2 + \frac{1}{16}x^3 \dots$$

$$\begin{aligned} E_{\pm} &= \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) \pm \frac{1}{2}(E_1^{(0)} - E_2^{(0)}) \left\{ 1 + \frac{4\varepsilon^2}{(E_1^{(0)} - E_2^{(0)})^2} \right\}^{1/2} \\ &= \frac{1}{2}(E_1^{(0)} + E_2^{(0)}) \pm \frac{1}{2}(E_1^{(0)} - E_2^{(0)}) \left\{ 1 + \frac{2\varepsilon^2}{(E_1^{(0)} - E_2^{(0)})^2} \dots \right\} \\ &\approx E_1^{(0)} - \left\{ \frac{\varepsilon^2}{\Delta E^{(0)}} \right\}, E_2^{(0)} + \left\{ \frac{\varepsilon^2}{\Delta E^{(0)}} \right\} \quad \Delta E^{(0)} = E_2^{(0)} - E_1^{(0)} \end{aligned}$$



Perturbation Theory

General non-degenerate system

- Assume many non-degenerate energy levels in system that we can solve

$$\hat{H}^{(0)} |n\rangle = E_n |n\rangle \quad n = 0, 1, 2, \dots$$

- Use parameter λ to keep track of the order of perturbation

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \dots$$

$$\Psi_0 = \Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \dots$$

$$E_0 = E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \dots$$

- Plug into Schrödinger equation and collect terms with same power of λ

$$\hat{H} \Psi_0 = E_0 \Psi_0$$

$$(\hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \dots)(\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \dots) =$$

$$(E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \dots)(\Psi_0^{(0)} + \lambda \Psi_0^{(1)} + \lambda^2 \Psi_0^{(2)} + \dots)$$

$$\{\hat{H}^{(0)}\Psi_0^{(0)} - E_0^{(0)}\Psi_0^{(0)}\} + \lambda\{\hat{H}^{(0)}\Psi_0^{(1)} + \hat{H}^{(1)}\Psi_0^{(0)} - E_0^{(0)}\Psi_0^{(1)} - E_0^{(1)}\Psi_0^{(0)}\} +$$

$$\lambda^2\{\hat{H}^{(0)}\Psi_0^{(2)} + \hat{H}^{(1)}\Psi_0^{(1)} + \hat{H}^{(2)}\Psi_0^{(0)} - E_0^{(0)}\Psi_0^{(2)} - E_0^{(1)}\Psi_0^{(1)} - E_0^{(2)}\Psi_0^{(0)}\} + \dots = 0$$

Perturbation Theory

Zeroth and first order energy corrections

- As parameter λ is arbitrary, each order of λ must be zero separately

$$\hat{H}^{(0)}\Psi_0^{(0)} = E_0^{(0)}\Psi_0^{(0)}$$

$$\{\hat{H}^{(0)} - E_0^{(0)}\}\Psi_0^{(1)} = \{E_0^{(1)} - \hat{H}^{(1)}\}\Psi_0^{(0)}$$

$$\{\hat{H}^{(0)} - E_0^{(0)}\}\Psi_0^{(2)} = \{E_0^{(2)} - \hat{H}^{(2)}\}\Psi_0^{(0)} + \{E_0^{(1)} - \hat{H}^{(1)}\}\Psi_0^{(1)}$$

- Zeroth-order term is same that we assumed was known
- First-order correction to wavefunction assuming complete set is linear combination

$$\Psi_0^{(1)} = \sum_n c_n \Psi_n^{(0)} = \sum_n c_n |n\rangle$$

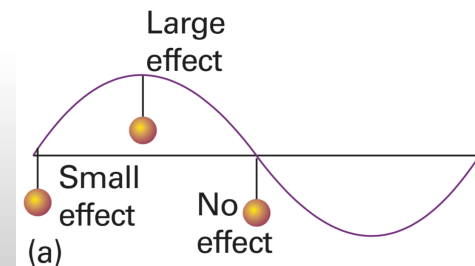
$$\sum_n c_n \{\hat{H}^{(0)} - E_0^{(0)}\} |n\rangle = \{E_0^{(1)} - \hat{H}^{(1)}\} |0\rangle$$

- Project onto eigenstate of interest and use orthonormalization conditions

$$\sum_n c_n \{E_n^{(0)} - E_0^{(0)}\} \langle 0 | n \rangle = \langle 0 | \{E_0^{(1)} - \hat{H}^{(1)}\} | 0 \rangle$$

$$E_0^{(1)} = \langle 0 | \hat{H}^{(1)} | 0 \rangle = H_{00}^{(1)}$$

- First-order energy is average of perturbation over unperturbed wavefunction



Perturbation Theory

Example

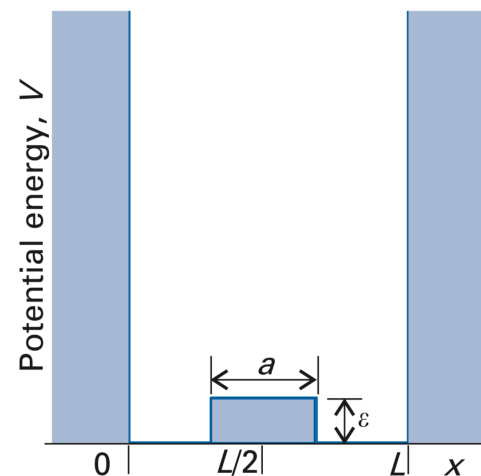
- What is the first order correction to the energy when a barrier of height ε and length $L/10$ is inserted into the center of the well for eigenstates a) $n=1$ and b) $n=2$?

$$H^{(1)} = \begin{cases} \varepsilon & \text{if } \frac{1}{2}(L-a) \leq x \leq \frac{1}{2}(L+a) \\ 0 & \text{otherwise} \end{cases}$$

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi}{L}x\right)$$

$$\int \sin^2(ax) dx = \frac{1}{2}x - \frac{1}{4a} \sin(2ax) + C$$

$$\sin(A \pm B) = \sin(A)\cos(B) \pm \cos(A)\sin(B)$$



$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}^{(1)} | \psi_n^{(0)} \rangle = \frac{2\varepsilon}{L} \int_{\frac{1}{2}(L-a)}^{\frac{1}{2}(L+a)} \sin^2\left(\frac{n\pi}{L}x\right) dx = \varepsilon \left\{ \frac{a}{L} - \frac{(-1)^n}{n\pi} \sin\left(\frac{n\pi a}{L}\right) \right\}$$

for $n=1$, $E_1^{(1)} = 0.1984\varepsilon$ for $n=2$, $E_2^{(1)} = 0.0065\varepsilon$

- Node at center of $n=2$ wavefunction so effect of perturbation less than that of $n=1$

Perturbation Theory

First-order wavefunction correction

- Determine coefficient that given zeroth order wavefunction contributes by projecting onto that wavefunction and using orthonormality conditions

$$\Psi_0^{(1)} = \sum_n c_n \Psi_n^{(0)} = \sum_n c_n |n\rangle$$

$$\sum_n c_n \langle k | \{E_n^{(0)} - E_0^{(0)}\} | n \rangle = \langle k | \{E_0^{(1)} - \hat{H}^{(1)}\} | 0 \rangle$$

$$c_k \{E_k^{(0)} - E_0^{(0)}\} = - \langle k | \hat{H}^{(1)} | 0 \rangle$$

$$c_k = \frac{H_{k0}^{(1)}}{\{E_0^{(0)} - E_k^{(0)}\}}$$

$$\Psi_0^{(1)} = \Psi_0^{(0)} + \sum_{k \neq 0} \left\{ \frac{H_{k0}^{(1)}}{E_0^{(0)} - E_k^{(0)}} \right\} \Psi_k^{(0)}$$

- Perturbation introduces **virtual transmissions** (is a linear superposition of unperturbed wavefunctions)

Perturbation Theory

Second-order energy correction

- Follows a similar procedure to evaluation of the first-order correction to the energy
- Second-order correction to wavefunction is also a (different) linear combination of zeroth-order wavefunctions

$$\Psi_0^{(2)} = \sum_n d_n \Psi_n^{(0)} = \sum_n d_n |n\rangle$$

- Substituting for first and second-order corrections to the wavefunction and projecting onto the zeroth-order state of interest

$$\{\hat{H}^{(0)} - E_0^{(0)}\} \Psi_0^{(2)} = \{E_0^{(2)} - \hat{H}^{(2)}\} \Psi_0^{(0)} + \{E_0^{(1)} - \hat{H}^{(1)}\} \Psi_0^{(1)}$$

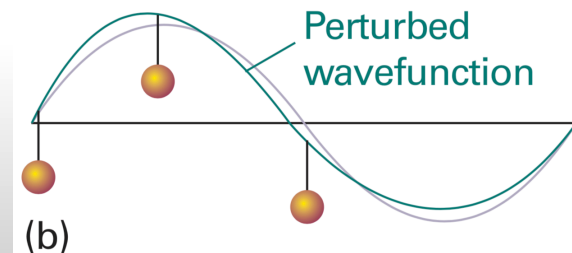
$$\sum_n d_n \{E_n^{(0)} - E_0^{(0)}\} \langle 0 | n \rangle = \langle 0 | \{E_0^{(2)} - \hat{H}^{(2)}\} | 0 \rangle + \langle 0 | \sum_n c_n \{E_0^{(1)} - \hat{H}^{(1)}\} | n \rangle$$

$$0 = E_0^{(2)} - \langle 0 | \hat{H}^{(2)} | 0 \rangle + c_0 \{E_0^{(1)} - \langle 0 | \hat{H}^{(1)} | 0 \rangle\} - \sum_{n \neq 0} c_n \langle 0 | \hat{H}^{(1)} | n \rangle$$

From 1st-order energy evaluation

- Rearranging for the second order energy and using the coefficients for the first-order correction to the wavefunction

$$E_0^{(2)} = H_{00}^{(2)} + \sum_{n \neq 0} \frac{H_{n0}^{(1)} H_{0n}^{(1)}}{\{E_0^{(0)} - E_n^{(0)}\}}$$



Perturbation Theory

Additional comments

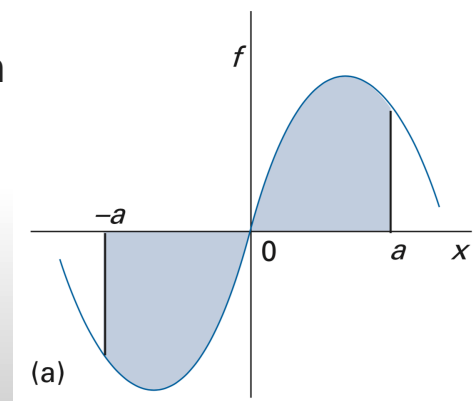
- The Hamiltonian matrix is hermitian so the numerator of the second order correction energy is quadratic and always positive
- If E_0 is the ground state, then all E_n are higher in energy and the second-order energy contribution is negative (lowers the energy)
- $2n+1$ rule says that if energy of order $2n+1$ is desired, we only need to know the wavefunction to order n

$$E_0^{(2)} = H_{00}^{(2)} - \sum_{n \neq 0} \frac{|H_{0n}^{(1)}|^2}{\Delta E^{(0)}}$$

n	0	1	2	3	4
2n+1	1	3	5	7	9

- The denominator is zero with degeneracies and the energy correction goes to infinity
 - Determine a new basis for zeroth-order wavefunctions (by taking a linear combination) such that effect of perturbation is as small as possible.
- Each matrix element is an integral which is only non-zero if it belongs to the totally symmetric irreducible representation

$$H_{0n}^{(1)} = \int \Psi_0^{(0)} \hat{H}^{(1)} \Psi_n^{(0)} d\tau \Rightarrow \Gamma^{(0)} \otimes \Gamma^{(p)} \otimes \Gamma^{(n)}$$



Variation Theory

Rayleigh ratio

- Guess a **trial wavefunction** — how good a guess is it? How can we improve the guess?
- Eigenfunctions of a Hermitian operator form a “complete set”
 - i.e. any function (including a wavefunction) can be written as a linear combination of eigenfunctions of Hermitian operator

$$|F\rangle = \sum_n c_n |f_n\rangle$$

- Vector analogy - eigenfunctions of Hermitian operator are basis vectors that “span the space” - any vector can be expressed using these basis vectors
- This implies that the eigenfunctions of Hermitian operator are “linearly independent” - they are orthogonal
- The Rayleigh ratio is the quantity obtained from

$$\mathcal{E} = \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

← approximate wavefunction

- We will show that for any trial wavefunction $\mathcal{E} \geq E_0$

Variation Theory

Proof of the variation theorem

- Exact wavefunctions are eigenfunctions of Hermitian operator

$$\hat{H}|\Psi_i\rangle = E|\Psi_i\rangle \longleftarrow \text{exact wavefunction}$$

- Complete set and so can use them to express approximate wavefunction

$$|\Phi\rangle = \sum_i c_i |\Psi_i\rangle$$

- Plugging expansion into Rayleigh ratio

$$\begin{aligned} \mathcal{E} &= \frac{\langle \Phi | \hat{H} | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \frac{\langle (\sum_i c_i \Psi_i) | \hat{H} | (\sum_j c_j \Psi_j) \rangle}{\langle (\sum_i c_i \Psi_i) | (\sum_j c_j \Psi_j) \rangle} \\ &= \frac{\sum_{ij} c_i^* c_j \langle \Psi_i | \hat{H} | \Psi_j \rangle}{\sum_{ij} c_i^* c_j \langle \Psi_i | \Psi_j \rangle} = \frac{\sum_{ij} c_i^* c_j E_j \langle \Psi_i | \Psi_j \rangle}{\sum_{ij} c_i^* c_j \langle \Psi_i | \Psi_j \rangle} \\ &= \frac{\sum_{ij} c_i^* c_j E_j \delta_{ij}}{\sum_{ij} c_i^* c_j \delta_{ij}} = \frac{\sum_i |c_i|^2 E_i}{\sum_j |c_j|^2} \geq E_0 \end{aligned}$$

Variation Theory

Rayleigh-Ritz method

- Write trial wavefunction as linear combination of basis (known) functions

$$|\Phi\rangle = \sum_i c_i |f_i\rangle$$

- The Rayleigh ratio is then

$$\mathcal{E} = \frac{\sum_{ij} c_i^* c_j H_{ij}}{\sum_{ij} c_i^* c_j S_{ij}}$$

- Find the minimum by differentiating with respect to each parameter and setting to 0

$$\begin{aligned} \frac{\partial \mathcal{E}}{\partial c_k} &= \frac{(\sum_{ij} c_i^* c_j S_{ij})(\sum_j c_j H_{kj} + \sum_i c_i^* H_{ik}) - (\sum_{ij} c_i^* c_j H_{ij})(\sum_j c_j S_{kj} + \sum_i c_i^* S_{ik})}{(\sum_{ij} c_i^* c_j S_{ij})^2} \\ &= \frac{(\sum_j c_j H_{kj} + \sum_i c_i^* H_{ik}) - \mathcal{E}(\sum_j c_j S_{kj} + \sum_i c_i^* S_{ik})}{(\sum_{ij} c_i^* c_j S_{ij})} \\ &= \frac{\sum_j c_j (H_{kj} - \mathcal{E} S_{kj}) + \sum_i c_i^* (H_{ik} - \mathcal{E} S_{ik})}{(\sum_{ij} c_i^* c_j S_{ij})} = 0 \end{aligned}$$

- Equation is satisfied if

$$\sum_j c_j (H_{kj} - \mathcal{E} S_{kj}) = 0$$

- Which gives the secular determinant to solve

$$|\mathbf{H} - \mathcal{E}\mathbf{S}| = 0$$



Summary

- Perturbation Theory
 - Time-independent perturbation theory
 - Two-level system
 - General system
 - First-order energy correction
 - First-order wavefunction correction
 - Second-order energy correction
 - Degeneracy, symmetry and $2n+1$ rule
- Variational principle
 - Rayleigh ratio
 - Rayleigh-Ritz method