A.2 Time-Independent Perturbation Theory

A. Approximation Method

- Express an unsolveable Hamiltonian as a modification to a solvable one

$$H = H^{(0)} + \lambda V^{(1)} \tag{1}$$

- Example: Hydrogen atom in an external electric field

$$H = \frac{p^2}{2m} - \frac{e^2}{r} + eE_z \tag{2}$$

- Desire

$$H|\phi_n\rangle = E_n|\phi_n\rangle \tag{3}$$

  ◇ Have the unperturbed solutions

$$H^{(0)}|\phi_n^{(0)}\rangle = E_n^{(0)}|\phi_n^{(0)}\rangle \tag{4}$$

  ◇ Look for power series solutions

$$|\phi_n\rangle = |\phi_n^{(0)}\rangle + \lambda|\phi_n^{(1)}\rangle + \lambda^2|\phi_n^{(2)}\rangle \ldots \tag{5}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \ldots \tag{6}$$

  ◇ Schrodinger Equation

$$\left(H^{(0)} + \lambda V^{(1)}\right)\left(|\phi_n^{(0)}\rangle + \lambda|\phi_n^{(0)}\rangle + \lambda^2|\phi_n^{(2)}\rangle \ldots\right) = \tag{7}$$

$$\left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} \ldots\right)\left(|\phi_n^{(0)}\rangle + \lambda|\phi_n^{(0)}\rangle + \lambda^2|\phi_n^{(2)}\rangle \ldots\right) \tag{8}$$

B. Non-degenerate

- Components of each power of λ must vanish separately
- Zeroth order

$$H^{(0)}|\phi_n^{(0)}\rangle = E_n^{(0)}|\phi_n^{(0)}\rangle$$

  ◇ No surprise here
  ◇ We will demand our perturbed states and energies reduce to the unperturbed case as $\lambda \to 0$

- First order

$$\left(H^{(0)} - E_n^{(0)} \right) |\phi_n^{(1)}\!> = \left(E_n^{(1)} - V^{(1)} \right) |\phi_n^{(0)}\!>$$

  ◇ Key: Expand $|\phi_n^{(1)}\!>$ in terms of the unperturbed basis

$$|\phi_n^{(1)}\!> = \sum_m c_{nm} |\phi_m^{(0)}\!>$$

  ◇ Trivially

$$H^{(0)} |\phi_n^{(1)}\!> = \sum_m c_{nm} E_m^{(0)} |\phi_m^{(0)}\!>$$

  ◇ Therefore, our first order equation becomes

$$\sum_m c_{nm} \left[E_m^{(0)} - E_n^{(0)} \right] |\phi_m^{(0)}\!> = \left(E_n^{(1)} - V^{(1)} \right) |\phi_n^{(0)}\!>$$

  ◇ Energy: Multiply by $<\!\phi_n^{(0)}|$

$$\sum_m c_{nm} \left[E_m^{(0)} - E_n^{(0)} \right] <\!\phi_n^{(0)}|\phi_m^{(0)}\!> = \; E_n^{(1)} - <\!\phi_n^{(0)}|V^{(1)}|\phi_n^{(0)}\!>$$

    ▲ LHS vanishes
    ▲ Define $V_{ij}^{(1)} = <\!\phi_i^{(0)}|V^{(1)}|\phi_j^{(0)}\!>$
    ▲ Therefore, $E_n^{(1)} = V_{nn}^{(1)}$
    ▲ First order correction

$$E_n = E_n^{(0)} + \lambda V_{nn}^{(1)} \tag{9}$$

  ◇ Eigenstate: Multiply $<\!\phi_\ell^{(0)}|$ with $\ell \neq n$

$$\sum_m c_{nm} \left(E_m^{(0)} - E_n^{(0)} \right) <\!\phi_\ell^{(0)}|\phi_m^{(0)}\!> = E_n^{(1)} <\!\phi_\ell^{(1)}|\phi_n^{(0)}\!> - V_{\ell n}^{(1)}$$

    ▲ $<\!\phi_\ell^{(0)}|\phi_m^{(0)}\!> = \delta_{\ell m}$
    ▲ $<\!\phi_\ell^{(0)}|\phi_n^{(0)}\!> = 0$

$$c_{\ell n} = \frac{-V_{\ell n}^{(1)}}{E_m^{(0)} - E_n^{(0)}}$$

▲ Therefore, to first order

$$|\phi_n\!> = |\phi_n^{(0)}\!> - \lambda \sum_{m\neq n} \frac{V_{mn}^{(1)}}{E_m^{(0)} - E_n^{(0)}} |\phi_m^{(0)}\!> \tag{10}$$

- 2nd Order
  - ◇ 2nd order is often necessary, because $V_{nn}^{(1)}$ often vanishes by symmetry
  - ◇ Schrodinger to 2nd order

$$\left(H^{(0)} - E_n^{(0)} \right) |\phi_n^{(2)}\!> + \left(V^{(1)} - E_n^{(1)} \right) |\phi_n^{(1)}\!> - E_n^{(2)} |\phi_n^{(0)}\!> = 0$$

  - ◇ Again, let $|\phi_n^{(2)}\!> = \sum_m d_{mn} |\phi_m^{(0)}\!>$

$$\sum_m d_{mn} \left(E_m^{(0)} - E_n^{(0)} \right) |\phi_m^{(0)}\!> + \sum_j c_{jn} \left(V^{(1)} - E_n^{(0)} \right) |\phi_j^{(0)}\!> - E_n^{(2)} |\phi_n^{(0)}\!> = 0$$

  - ◇ Energies: Apply $<\!\phi_n^{(0)}|$

$$\sum_j c_{jn} \left(V_{nj}^{(1)} - E_n^{(0)} \delta_{nj} \right) = E_n^{(2)}$$

$$E_n^{(2)} = - \sum_{j\neq n} \frac{\left| V_{jn}^{(1)} \right|^2}{E_j^{(0)} - E_n^{(0)}} \tag{11}$$

  - ◇ Wave function: Apply $<\!\phi_k^{(0)}|$

$$d_{kn} = \frac{V_{nn}^{(1)} V_{kn}^{(1)}}{\left(E_k^{(0)} - E_n^{(0)} \right)^2} - \sum_{\ell\neq n} \frac{V_{\ell n}^{(1)} V_{kn}^{(1)}}{\left(E_\ell^{(0)} - E_n^{(0)} \right) \left(E_k^{(0)} - E_n^{(0)} \right)}$$

C. Degenerate, unperturbed states

- In this case, our c_{jn} coefficientes will 'blow up' for the degenerate states
- Perturbation will generally lift the degeneracy
- Approach:
  - ◇ Find the linear combinations of $\phi_i^{(0)}$ that diagonalize $V^{(1)}$
  - ◇ First order energy correction is $< V^{(1)} >$ for these states
- Brute force: Express ϕ_n in terms of a sum of the degenerate states

◇ Proceed as before, taking powers of λ

$$|\phi_n> = \sum_i c_i|\phi_i^{(0)}> + \lambda|\phi_n^{(1)}> + \lambda^2|\phi_n^{(2)}> + \ldots$$

- Consider a two-fold case (for simplicity)

$$|\phi> = c_1|\phi_1^{(0)}> + c_2|\phi_2^{(0)}> + \lambda|\phi_n^{(1)}> + \ldots$$

  ◇ First order

$$V^{(1)}\left(c_1\phi_1^{(0)} + c_2\phi_2^{(0)}\right) + H^{(0)}|\phi^{(1)}> = E^{(1)}\left(c_1\phi_1^{(0)} + c_2\phi_2^{(0)}\right) + E^{(0)}|\phi^{(1)}>$$

  ◇ Apply $<\phi_1^{(0)}|$ and $<\phi_2^{(0)}|$ to obtain 2 equations for the two unknowns c_1, c_2

$$c_1(V_{11}^{(1)} - E^{(1)}) + c_2V_{21}^{(1)} = 0 \tag{12}$$

$$c_1V_{21}^{(1)} + c_2(V_{22}^{(1)} - E^{(1)}) = 0 \tag{13}$$

  ◇ Linear algebra: Require

$$\begin{vmatrix} V_{11}^{(1)} - E^{(1)} & V_{12}^{(1)} \\ V_{21}^{(1)} & V_{22}^{(1)} - E^{(1)} \end{vmatrix} = 0 \tag{14}$$

    ▲ We have diagnolized the potential in the degenerate subspace
    ▲ Eigenvalues give the first order energy corrections

- Symmetry 'shortcut'
  ◇ There must exist at least one other operator that commutes with $H^{(0)}$ which distinguishes the unperturbed degenerate states
  ◇ If one of these operators A commutes with $V^{(1)}$, then the simultaneous eigenstates of A, H will automatically diagonalize $V^{(1)}$
  ◇ Two state case

$$A|\phi_1^{(0)}> = a_1|\phi_1^{(0)}>$$

$$A|\phi_2^{(0)}> = a_2|\phi_2^{(0)}>$$

    ▲ $a_1 \neq a_2$
    ▲ $[A, V^{(1)}] = 0$
    ▲ We find

$$<\phi_1^{(0)}|[A, V^{(1)}]|\phi_2^{(0)}> = 0 = (a_1 - a_2)V_{12}^{(1)}$$

$$\Rightarrow V_{12}^{(1)} = 0 \qquad \text{as desired}$$

A.3 Time-dependent Perturbation Theory

A. Hamiltonian

- Usual perturbation

$$H = H^{(0)} + \lambda V^{(1)} \tag{15}$$

- Assume $H^{(0)}$ does not depend explicitly on time
  - ◇ Known eigenstates

$$H^{(0)}|\phi_n\!> = E_n|\phi_n\!>$$

  - ◇ Unperturbed states may be degenerate

B. Time-evolution

- Arbitrary state at $t = t_0 = 0$

$$|\alpha, t_0; t_0\!> = \sum_n c_n|\phi_n\!>$$

- Time t

$$\begin{aligned} |\alpha, t_0; t\!> &= \mathcal{U}(t, t_0)\sum_n c_n(t)|\phi_n\!> \\ &= \sum_n c_n(t)\mathrm{e}^{-iE_nt/\hbar}\,|\phi_n\!> \end{aligned}$$

- Seek equations for $c_n(t)$
- Probability
  - ◇ Identify $|c_n(t)|^2$ as the probability that $|\alpha\!>$ is in the state $|\phi_n\!>$ at time t
  - ◇ Conserving probability

$$|\!<\!\alpha(t)|\alpha(t)\!>\!|^2 = 1 \;\Rightarrow\; \sum_n |c_n(t)|^2 = 1 \tag{16}$$

  - ◇ Transition probability: Probability in state n at $t = 0$ to be in state m at time t

$$P_{nm} = |c_m(t)|^2 \tag{17}$$

  - ◇ Initial condition

$$c_m(0) = \delta_{mn} \tag{18}$$

C. Schrodinger Equation

$$H|\alpha\!> = i\hbar\frac{\partial}{\partial t}|\alpha\!>$$

- Expanding $|\alpha\!>$ as above

$$\sum_n c_n(t)\mathrm{e}^{-iE_nt/\hbar}H|\phi_n\!> = i\hbar\sum_n \dot{c}_n(t)\mathrm{e}^{-iE_nt/\hbar}|\phi_n\!> + \sum_n c_n(t)E_n\mathrm{e}^{-iE_nt/\hbar}|\phi_n\!>$$

- Multiply by $<\!\phi_f(t)| = <\!\phi_f|\mathrm{e}^{iE_ft/\hbar}$

$$\lambda\sum_n c_n(t)\!<\!\phi_f|V^{(1)}|\phi_n\!>\!\mathrm{e}^{i(E_f-E_n)t/\hbar} = i\hbar\dot{c}_f(t)$$

  - ◇ This only follows if

$$[V^{(1)},\mathcal{U}] = 0$$

  - ◇ Define

$$\omega_{fn} \equiv \frac{E_f - E_n}{\hbar}$$
$$V_{fn} \equiv <\!\phi_f|V^{(1)}|\phi_n\!>$$

  - ◇ Finally

$$i\hbar\dot{c}_f(t) = \lambda\sum_n c_n(t)V_{fn}\mathrm{e}^{i\omega_{fn}t} \tag{19}$$

D. Expand $c_n(t)$

- First term

$$c_n(t) = c_n^{(0)} + \lambda c_n^{(1)}(t) \tag{20}$$

- The Schrodinger equation becomes

$$i\hbar\dot{c}_n^{(0)} + i\hbar\lambda\dot{c}_n^{(1)} = \lambda\sum_n V_{fn}\mathrm{e}^{i\omega_{fn}t}\left[\,c_n^{(0)} + \lambda c_n^{(1)}\,\right]$$

- Zeroth order in λ

$$i\hbar\dot{c}_n^{(0)} = 0 \tag{21}$$
$$\Rightarrow\ c_n^{(0)}(t) = \delta_{ni} \tag{22}$$

- First order in λ

$$i\hbar\dot{c}_f^{(1)} = V_{fi}\mathrm{e}^{i\omega_{fi}t} \tag{23}$$

$$\Rightarrow \; c_f(t) = \frac{1}{i\hbar}\int\limits_0^t \mathrm{e}^{i\omega_{fi}t}V_{fi}(t)dt \tag{24}$$

- Assume the perturbation is 'pulsed'

$$V^{(1)} = 0 \quad \text{for } t < 0 \text{ and } t > \mathcal{T}$$

  ◇ Solution for $c_n^{(1)}$ at $t > \mathcal{T}$

$$c_n^{(1)}(t > \mathcal{T}) = \frac{1}{i\hbar}\int\limits_{-\infty}^{\infty} dt\ \mathrm{e}^{i\omega_{fi}t}V_{fi}(t) \tag{25}$$

  ◇ Fourier transform

$$V_{fi}(\omega) \equiv \frac{1}{2\pi}\int\limits_{-\infty}^{\infty} dt\ \mathrm{e}^{i\omega t}V_{fi}(t)$$

$$c_f(t > \mathcal{T}) = \frac{2\pi}{i\hbar}V_{fi}(\omega_{fi}) \tag{26}$$

- Transition Probability

$$P_{fi} = \frac{4\pi^2}{\hbar^2}\Big|V_{fi}(\omega_{fi})\Big|^2 \tag{27}$$

  ◇ Fermi's Golden rule

  ◇ To calculate the transition probability to a state with energy E_f, simply sum equation 27 over the eigenfucntions with $E = E_f$