The time-independent and time-dependent perturbation method

- The time-independent perturbation method
- The time-dependent perturbation method

References

The material reviewed here is standard and can be found in any Quantum Mechanics textbook and in brief in several of the electronic structure calculations books.

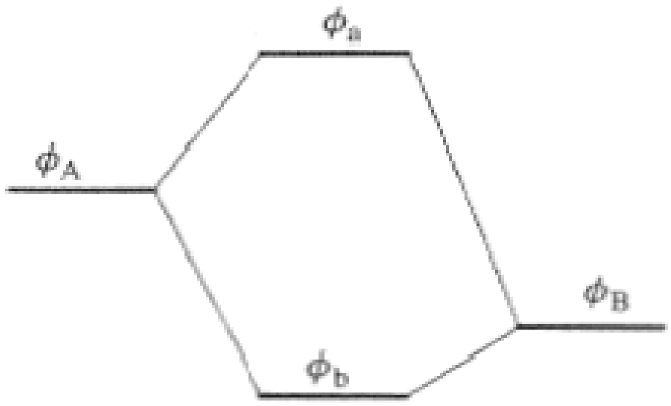
Recommended reading material for these slides is given below:

- Principles of Quantum Mechanics, by R. Shankar
- Introduction to Quantum Mechanics, D. J. Griffiths
- Quantum Mechanics, B. H. Bransden and C.J. Joachain
- Methods of Electronic-Structure Calculations, M. Springborg

The perturbation method

- The idea behind the perturbation method is that we know the wavefunctions and eigenvalues for some given system (often through the variational method) and want to include the ``small'' effects of some extra interaction.

- For example, consider how the energy levels of two non-interacting atoms or molecules A and B will change when they come close to each other (assuming weak interaction).



- The interaction here between A and B is introduced as a perturbation.

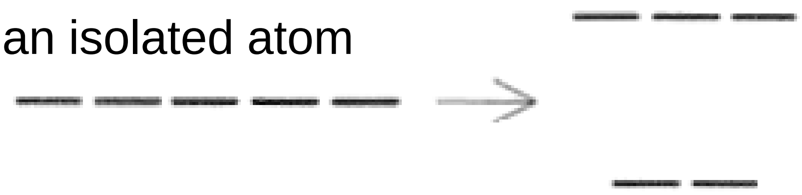
The perturbation method: An example

- Consider an isolated transition-metal atom from the *3d* series (e.g., Ti, V, Fe, Cr, . . .). Neglecting spin we have five *3d* orbitals that are energetically degenerate as shown in the left part of the fig. below.

  These 3d orbitals are very compact (close to the nucleus)

- We now place the atom in a position of high cubic symmetry in a crystal. The atom now feels a perturbation from the surrounding crystal (its symmetry is lowered from spherical in the isolated atom to cubic in the crystal).
  The orbitals split as shown on the right of the Fig. below.

$$\hat{H} = \hat{H}_0 + \Delta\hat{H},$$



five *3d* orbitals
in an isolated atom

The orbitals
split when placing
the atom in a crystal

The perturbation method

- We assume a perturbation to the Hamiltonian as follows:

$$\hat{H} = \hat{H}_0 + \Delta\hat{H} \quad \text{with} \quad \Delta\hat{H} \ll \hat{H}_0,$$

- For example for the case of the 2 atoms $\hat{H}_0$ is the sum of the two Hamiltonians of the isolated atoms (no interactions) and $\Delta\hat{H}$ is the induced small interactions when the atoms come close.

- ``Smallness'' of the perturbation is defined in the following sense:

$$\langle\phi|\Delta\hat{H}|\phi\rangle \ll \langle\phi|\hat{H}_0|\phi\rangle$$

for ``some'' orbitals ϕ of interest.

The perturbation method

- Let's re-write the perturbation as:

$$\hat{H} = \hat{H}_0 + \lambda \hat{H}_1, \quad \text{with} \quad \Delta \hat{H} = \lambda \hat{H}_1 \quad \text{and} \quad |\lambda| \ll 1.$$

- We assume we know the solution of the unperturbed problem:

$$\hat{H}_0 \psi_i^{(0)} = E_i^{(0)} \psi_i^{(0)}, \qquad \langle \psi_i^{(0)} | \psi_j^{(0)} \rangle = \delta_{i,j},$$

- We are interested in a single of this orbital (e.g. the ground state) and how it changes when the perturbation is turned on. Let's work with the kth orbital:

$$\hat{H}_0 \psi_k^{(0)} = E_k^{(0)} \psi_k^{(0)} \qquad E_i^{(0)} \neq E_k^{(0)} \quad \text{for} \quad i \neq k.$$

Non degenerate

Non-degenerate perturbation theory

- We seek a solution to the following equation:

$$\hat{H}\psi_k = (\hat{H}_0 + \lambda \hat{H}_1)\psi_k = E_k \psi_k$$

- Since the eigenfunctions of the unperturbed problem form a complete set, we can write (with the coefficients c_i being unknown):

$$\psi_k = \sum_i c_i \psi_i^{(0)}$$

- We expand E_k and c_i in powers of the perturbation parameter λ as follows:

$$E_k = E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots$$

$$c_i = c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots$$

Non-degenerate perturbation theory

- Recall that for $\lambda = 0$ (unperturbed problem), we are at the k^{th} state, thus

$$c_i^{(0)} = \delta_{i,k}$$

- Substitution into $\hat{H}\psi_k = (\hat{H}_0 + \lambda \hat{H}_1)\psi_k = E_k \psi_k$ results in:

$$(\hat{H}_0 + \lambda \hat{H}_1) \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\psi_i^{(0)}$$

$$= [E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots] \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\psi_i^{(0)}$$

- We now follow the algebra and expand this equation further as shown next.

Non-degenerate perturbation theory

- The left side of the previous equ. becomes:

$$\hat{H}_0 \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\psi_i^{(0)}$$

$$+ \lambda \hat{H}_1 \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\psi_i^{(0)}$$

$$= \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\hat{H}_0 \psi_i^{(0)}$$

$$+ \lambda \hat{H}_1 \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\psi_i^{(0)}$$

$$= \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]E_i^{(0)} \psi_i^{(0)}$$

$$+ \lambda \hat{H}_1 \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\psi_i^{(0)}.$$

Non-degenerate perturbation theory

- Substituting this to the left of

$$(\hat{H}_0 + \lambda \hat{H}_1) \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] \psi_i^{(0)}$$

$$= [E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots] \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] \psi_i^{(0)}$$

- Multiplying both sides with $[\psi_l^{(0)}]^*$ and integrating over all space results in

$$\sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] E_i^{(0)} \langle \psi_l^{(0)} | \psi_i^{(0)} \rangle$$

$$+ \lambda \left\langle \psi_l^{(0)} \middle| \hat{H}_1 \middle| \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] \psi_i^{(0)} \right\rangle$$

$$= [E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots]$$

$$\times \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] \langle \psi_l^{(0)} | \psi_i^{(0)} \rangle.$$

Non-degenerate perturbation theory

- Using the orthonormality of the unperturbed eigenfunctions, we simplify as:

$$\begin{aligned}
&[c_l^{(0)} + \lambda c_l^{(1)} + \lambda^2 c_l^{(2)} + \cdots]E_l^{(0)} \\
&\qquad + \lambda \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle \\
&\quad = [E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots][c_l^{(0)} + \lambda c_l^{(1)} + \lambda^2 c_l^{(2)} + \cdots].
\end{aligned}$$

- The coefficients on the left and right sides for each power term λ^n should be equal.

- λ^0 term (for the case *l=k)*: $E_k^{(0)} = E_k^{(0)}$ -- this is trivially satisfied

Non-degenerate perturbation theory

$$
\begin{aligned}
&[c_l^{(0)} + \lambda c_l^{(1)} + \lambda^2 c_l^{(2)} + \cdots]E_l^{(0)} \\
&\qquad + \lambda \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots]\langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle \\
&\quad = [E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots][c_l^{(0)} + \lambda c_l^{(1)} + \lambda^2 c_l^{(2)} + \cdots].
\end{aligned}
$$

- λ^1 term: $c_l^{(1)} E_l^{(0)} + \sum_i c_i^{(0)} \langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle = E_k^{(0)} c_l^{(1)} + E_k^{(1)} c_l^{(0)}$

- λ^2 term: $c_l^{(2)} E_l^{(0)} + \sum_i c_i^{(1)} \langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle = E_k^{(0)} c_l^{(2)} + E_k^{(1)} c_l^{(1)} + E_k^{(2)} c_l^{(0)}$

Non-degenerate perturbation theory

- λ^1 term: $$c_l^{(1)}E_l^{(0)} + \sum_i c_i^{(0)}\langle\psi_l^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle = E_k^{(0)}c_l^{(1)} + E_k^{(1)}c_l^{(0)}$$

- For the case *l*=*k*, we derive from this equation the following (recall $c_i^{(0)} = \delta_{i,k}$):

$$c_k^{(1)}E_k^{(0)} + \langle\psi_k^{(0)}|\hat{H}_1|\psi_k^{(0)}\rangle = E_k^{(0)}c_k^{(1)} + E_k^{(1)}.$$

- From this equation we can then write: $E_k^{(1)} = \langle\psi_k^{(0)}|\hat{H}_1|\psi_k^{(0)}\rangle.$

- Thus

$$\begin{aligned} E_k &= E_k^{(0)} + \lambda E_k^{(1)} + \cdots \\ &= E_k^{(0)} + \lambda\langle\psi_k^{(0)}|\hat{H}_1|\psi_k^{(0)}\rangle + \cdots \\ &= E_k^{(0)} + \langle\psi_k^{(0)}|\lambda\hat{H}_1|\psi_k^{(0)}\rangle + \cdots \\ &= E_k^{(0)} + \langle\psi_k^{(0)}|\Delta\hat{H}|\psi_k^{(0)}\rangle + \cdots. \end{aligned}$$

Non-degenerate perturbation theory

- λ^1 term: $$c_l^{(1)} E_l^{(0)} + \sum_i c_i^{(0)} \langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle = E_k^{(0)} c_l^{(1)} + E_k^{(1)} c_l^{(0)}$$

- For the case $l \neq k$, we derive from this equation the following:

$$c_l^{(1)} E_l^{(0)} + \langle \psi_l^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle = E_k^{(0)} c_l^{(1)} \quad \Rightarrow \quad c_l^{(1)} = \frac{\langle \psi_l^{(0)} | \hat{H}_1 | \psi_k^{(0)} \rangle}{E_k^{(0)} - E_l^{(0)}}.$$

- Note that we use the assumption here that the k^th^ state is non-degenerate!

Non-degenerate perturbation theory

- Let's normalize the computed kth perturbed eigenfunction (up to order λ^1)

$$\begin{aligned}\langle\psi_k|\psi_k\rangle &\simeq \left\langle \sum_i (c_i^{(0)} + \lambda c_i^{(1)})\psi_i^{(0)} \middle| \sum_j (c_j^{(0)} + \lambda c_j^{(1)})\psi_j^{(0)} \right\rangle \\ &= \sum_{i,j} (c_i^{(0)} + \lambda c_i^{(1)})^* (c_j^{(0)} + \lambda c_j^{(1)}) \langle \psi_i^{(0)} | \psi_j^{(0)} \rangle \\ &= \sum_i (c_i^{(0)} + \lambda c_i^{(1)})^* (c_i^{(0)} + \lambda c_i^{(1)}) \\ &= (1 + \lambda c_k^{(1)})^* (1 + \lambda c_k^{(1)}) + \sum_{i \neq k} \lambda^2 |c_i^{(1)}|^2 .\end{aligned}$$

- Neglecting quadratic terms in λ, we note that this is normalized ONLY if:

$$c_k^{(1)} = 0.$$

2^{nd} order correction

- Recall the λ^2 term in our expansion:

$$c_l^{(2)}E_l^{(0)} + \sum_i c_i^{(1)}\langle\psi_l^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle = E_k^{(0)}c_l^{(2)} + E_k^{(1)}c_l^{(1)} + E_k^{(2)}c_l^{(0)}$$

- Taking the special case *l*=*k*, we derive the following:

$$c_k^{(2)}E_k^{(0)} + \sum_i c_i^{(1)}\langle\psi_k^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle = c_k^{(2)}E_k^{(0)} + c_k^{(1)}E_k^{(1)} + E_k^{(2)} \qquad \Rightarrow$$

$$E_k^{(2)} = \sum_i c_i^{(1)}\langle\psi_k^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle - c_k^{(1)}E_k^{(1)} \qquad = \sum_{i\neq k} c_i^{(1)}\langle\psi_k^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle$$

$$= \sum_{i\neq k} \frac{\langle\psi_i^{(0)}|\hat{H}_1|\psi_k^{(0)}\rangle}{E_k^{(0)} - E_i^{(0)}}\langle\psi_k^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle \qquad = \sum_{i\neq k} \frac{|\langle\psi_i^{(0)}|\hat{H}_1|\psi_k^{(0)}\rangle|^2}{E_k^{(0)} - E_i^{(0)}}$$

Final solution

- Energy of the perturbed kth state up to 2nd order

$$E_k = E_k^{(0)} + \langle\psi_k^{(0)}|\Delta\hat{H}|\psi_k^{(0)}\rangle + \sum_{i\neq k}\frac{|\langle\psi_i^{(0)}|\Delta\hat{H}|\psi_k^{(0)}\rangle|^2}{E_k^{(0)} - E_i^{(0)}}$$

- Perturbed kth state up to 1st order

$$\psi_k = \psi_k^{(0)} + \sum_{i\neq k}\frac{\langle\psi_i^{(0)}|\Delta\hat{H}||\psi_k^{(0)}\rangle}{E_k^{(0)} - E_i^{(0)}}\psi_i^{(0)}.$$

The degenerate perturbation case

- We assumed up to now that there was no other (unpurturbed) orbital with the same energy as that of the kth unperturbed state

- We now assume that we have a number of unperturbed orbitals with the same eigenvalue. We define a linear combination of these as follows (‘ here refers to

  summation on the degenerate orbitals *j* for which $E_j^{(0)} = E_k^{(0)}$)

$$\tilde{\psi}_k^{(0)} = \sum_j{}' a_j \psi_j^{(0)}.$$

- Recall that in the non-degerate case we wrote

$$\psi_k = \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] \psi_i^{(0)}.$$

with the constraint $c_i^{(0)} = \delta_{i,k}.$

The degenerate perturbation case

- We here enforce the following constraint (for the j's in the ' set): $a_j = c_j^{(0)}$

$$\tilde{\psi}_k^{(0)} = {\sum_j}' a_j \psi_j^{(0)}. \qquad \psi_k = \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] \psi_i^{(0)}.$$

- We start again from the following (earlier derived equation)

$$\begin{aligned}
&[c_l^{(0)} + \lambda c_l^{(1)} + \lambda^2 c_l^{(2)} + \cdots] E_l^{(0)} \\
&\qquad + \lambda \sum_i [c_i^{(0)} + \lambda c_i^{(1)} + \lambda^2 c_i^{(2)} + \cdots] \langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle \\
&\quad = [E_k^{(0)} + \lambda E_k^{(1)} + \lambda^2 E_k^{(2)} + \cdots][c_l^{(0)} + \lambda c_l^{(1)} + \lambda^2 c_l^{(2)} + \cdots].
\end{aligned}$$

- λ^1 term: $c_l^{(1)} E_l^{(0)} + \sum_i c_i^{(0)} \langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle = E_k^{(0)} c_l^{(1)} + E_k^{(1)} c_l^{(0)}$

The degenerate perturbation case

- λ^1 term: $$c_l^{(1)} E_l^{(0)} + \sum_i c_i^{(0)} \langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle = E_k^{(0)} c_l^{(1)} + E_k^{(1)} c_l^{(0)}$$

- The only non-zero coefficients $c_j^{(0)}$ are those that satisfy $a_j = c_j^{(0)}$

We then simplify as:

$$c_l^{(1)} E_l^{(0)} + {\sum_i}' c_i^{(0)} \langle \psi_l^{(0)} | \hat{H}_1 | \psi_i^{(0)} \rangle = E_k^{(0)} c_l^{(1)} + E_k^{(1)} c_l^{(0)}$$

- The function $\psi_l^{(0)}$ was arbitrarily chosen, so it can be any of the functions for which $E_l^{(0)} = E_k^{(0)}$

The degenerate perturbation case

$$c_l^{(1)}E_l^{(0)} + \sum_i{}' c_i^{(0)}\langle\psi_l^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle = E_k^{(0)}c_l^{(1)} + E_k^{(1)}c_l^{(0)}$$

- The function $\psi_l^{(0)}$ was arbitrarily chosen, so can take it as any of the functions for which $E_l^{(0)} = E_k^{(0)}$. This gives the following:

$$\sum_i{}' c_i^{(0)}\langle\psi_l^{(0)}|\hat{H}_1|\psi_i^{(0)}\rangle = E_k^{(1)}c_l^{(0)}$$

which is a matrix eigenvalue problem of the form: $\underline{\underline{H}}_1 \cdot \underline{c}^{(0)} = E_k^{(1)} \cdot \underline{c}^{(0)}$

- The size of the matrix $\underline{\underline{H}}_1$ is equal to the number of degenerate eigenfunctions

$$E_k = E_k^{(0)} + \lambda E_k^{(1)} + \cdots \qquad \bar{\psi}_k^{(0)} = \sum_i{}' c_i^{(0)}\psi_i^{(0)}.$$

Where does this degerate case is useful?

- Consider an isolated atom with one electron that can occupy 3 *p*-orbitals, i.e. the p_x, p_y and p_z orbitals. These are degenerate orbitals (have the same energy). Any combination of them (in other directions) can serve as alternative p orbitals.

- If we introduce a small perturbation in the Hamiltonian in the z-axis, we would expect that only the p_z orbital will be perturbed by a small amount with the p_x and p_y orbitals remaining unpurturbed.

- If we had based our calculations on alternative p orbitals we would have to form linear combinations of those so that one of them becomes the p_z orbital – if we don’t do that, application of the perturbation theory will not be appropriate as the induced perturbation in the alternative orbitals may result in a perturbation in the z-axis that is not small!

- The main difficulty of course is how to choose these linear combinations that will make application of the perturbation approach reasonable.

Time-dependent perturbation theory

- We consider the time-dependent Schrödinger equation

$$\hat{H}\psi(\vec{x},t) = i\hbar\frac{\partial}{\partial t}\psi(\vec{x},t)$$

- Consider a perturbation $\hat{H} = \hat{H}_0 + \Delta\hat{H}(t)$

- We assume we know the solution of the unperturbed time-dependent Schrödinger equation

$$\hat{H}_0\tilde{\psi}_k^{(0)}(\vec{x}) = E_k^{(0)}\tilde{\psi}_k^{(0)}(\vec{x})$$

The time-dependent solution corresponding to this is of course given as

$$\psi_k^{(0)}(\vec{x},t) = \tilde{\psi}_k^{(0)}(\vec{x})\exp\left(-\frac{iE_k^{(0)}t}{\hbar}\right)$$

Time-dependent perturbation theory

- We write the time-dependent wave functions as

$$\psi_k(\vec{x}, t) = \sum_i c_i(t)\psi_i^{(0)}(\vec{x}, t).$$

- Substitution into the time-dependent Schrödinger equation gives:

$$[\hat{H}_0 + \Delta\hat{H}(t)]\sum_i c_i(t)\psi_i^{(0)}(\vec{x}, t) = i\hbar\frac{\partial}{\partial t}\sum_i c_i(t)\psi_i^{(0)}(\vec{x}, t),$$

- The above equation is simplified as follows:

$$\sum_i c_i(t)E_i^{(0)}\psi_i^{(0)}(\vec{x}, t) + \Delta\hat{H}(t)\sum_i c_i(t)\psi_i^{(0)}(\vec{x}, t)$$

$$= i\hbar\sum_i\left[\frac{\partial c_i(t)}{\partial t} - \frac{iE_i^{(0)}}{\hbar}c_i(t)\right]\psi_i^{(0)}(\vec{x}, t),$$

Time-dependent perturbation theory

$$\sum_i c_i(t)E_i^{(0)}\psi_i^{(0)}(\vec{x},t) + \Delta\hat{H}(t)\sum_i c_i(t)\psi_i^{(0)}(\vec{x},t)$$

$$= \mathrm{i}\hbar\sum_i\left[\frac{\partial c_i(t)}{\partial t} - \frac{\mathrm{i}E_i^{(0)}}{\hbar}c_i(t)\right]\psi_i^{(0)}(\vec{x},t),$$

- This is simplified further as:

$$\Delta\hat{H}(t)\sum_i c_i(t)\psi_i^{(0)}(\vec{x},t) = \mathrm{i}\hbar\sum_i \frac{\partial c_i(t)}{\partial t}\psi_i^{(0)}(\vec{x},t)$$

- We multiply this equation with $[\psi_j^{(0)}(\vec{x},t)]^*$ (*j*=arbitrary) and integrate over all space

$$\mathrm{i}\hbar\frac{\mathrm{d}c_j(t)}{\mathrm{d}t} = \sum_i \langle\tilde{\psi}_j^{(0)}|\Delta\hat{H}(t)|\tilde{\psi}_i^{(0)}\rangle \exp(\mathrm{i}\omega_{ji}t)c_i(t)$$ where $$\omega_{ji} = \frac{E_j^{(0)} - E_i^{(0)}}{\hbar}$$

Time-dependent perturbation theory

$$i\hbar\frac{\mathrm{d}c_j(t)}{\mathrm{d}t} = \sum_i \langle\tilde{\psi}_j^{(0)}|\Delta\hat{H}(t)|\tilde{\psi}_i^{(0)}\rangle \exp(\mathrm{i}\omega_{ji}t)c_i(t)$$ where $$\omega_{ji} = \frac{E_j^{(0)} - E_i^{(0)}}{\hbar}$$

- Substituting $\Delta\hat{H}(t) = \lambda\hat{H}_1(t)$ and expanding the coefficients $c_i(t)$ as

$$c_i(t) = c_i^{(0)}(t) + \lambda c_i^{(1)}(t) + \lambda^2 c_i^{(2)}(t) + \cdots.$$

- λ^0 term: $$i\hbar\frac{\mathrm{d}c_j^{(0)}(t)}{\mathrm{d}t} = 0$$

- λ^n term (note that $\Delta\hat{H}$ has already a λ on it!):

$$i\hbar\frac{\mathrm{d}c_j^{(n)}(t)}{\mathrm{d}t} = \sum_i \langle\tilde{\psi}_j^{(0)}|\Delta\hat{H}(t)|\tilde{\psi}_i^{(0)}\rangle \exp(\mathrm{i}\omega_{ji}t)c_i^{(n-1)}(t).$$

Time-dependent perturbation theory

- Consider the following case: $c_j(t) = \delta_{j,k} \quad \text{for} \quad t < t_0.$

- This implies that the perturbation is turned on at time t_0 and the state before the perturbation was turned on is labeled as state k.

$$i\hbar \frac{\mathrm{d}c_j^{(0)}(t)}{\mathrm{d}t} = 0 \quad \Rightarrow \quad c_j^{(0)}(t) = \delta_{j,k}$$

$$i\hbar \frac{\mathrm{d}c_j^{(n)}(t)}{\mathrm{d}t} = \sum_i \langle \tilde{\psi}_j^{(0)} | \Delta \hat{H}(t) | \tilde{\psi}_i^{(0)} \rangle \exp(\mathrm{i}\omega_{ji} t) c_i^{(n-1)}(t). \quad \Rightarrow$$

$$c_j^{(1)}(t) = \frac{1}{i\hbar} \int_{t_0}^{t} \langle \tilde{\psi}_j^{(0)} | \Delta \hat{H}(t') | \tilde{\psi}_k^{(0)} \rangle \exp(\mathrm{i}\omega_{jk} t')\, \mathrm{d}t'$$

Time-dependent perturbation theory

- Note that in an external time-dependent perturbation, orbitals that were unoccupied before the perturbation was turned on may become occupied and also that the populations may become time-dependent including oscillating.

- Special cases of the above examined in many quantum mechanics books include perturbations of very short or very long durations.