Time Dependent Wave Equation
Quantum Mechanical Description

Hamiltonian
Static/Time-dependent

Time-dependent Energy operator

\[ \left\{ \hat{H}_0 + \hat{H}(t) \right\} \Psi(t) = i\hbar \frac{\partial \Psi(t)}{\partial t} \]

The Hamiltonian and wavefunction are time-dependent
There is a relationship between time-dependent and static wave functions.

The total Hamiltonian is composed of two parts:

\[ H_{\text{total}} = H_0 + H(t) \]

\[ \Psi(t) = \Psi e^{-iH_{\text{total}}t/\hbar} \]

We can use the time-dependent Hamiltonian to connect static wavefunctions of different states.
The transition probability calculated using the Fermi Golden Rule

\[ P_{12} = \frac{\langle \Psi_1 | H | \Psi_2 \rangle^2 \sin^2 \left( \frac{\omega - \omega_{12}}{2} t \right)}{4\hbar^2 \left( \frac{\omega - \omega_{12}}{2} \right)^2} \]

This expression is derived using time-dependent perturbation theory. It is valid for a number of time-dependent processes that involve transitions between states 1 and 2. The rate constant \( k_{12} = P_{12}/t \).
The Fermi Golden Rule can be used to calculate many types of transitions

<table>
<thead>
<tr>
<th>Transition</th>
<th>H(t) dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Optical transitions</td>
<td>Electric field</td>
</tr>
<tr>
<td>2. NMR transitions</td>
<td>Magnetic field</td>
</tr>
<tr>
<td>3. Electron transfer</td>
<td>Non-adiabaticity</td>
</tr>
<tr>
<td>4. Energy transfer</td>
<td>Dipole-dipole</td>
</tr>
<tr>
<td>5. Atom transfer</td>
<td>Non-adiabaticity</td>
</tr>
<tr>
<td>6. Internal conversion</td>
<td>Non-adiabaticity</td>
</tr>
<tr>
<td>7. Intersystem crossing</td>
<td>Spin-orbit coupling</td>
</tr>
</tbody>
</table>
Optical electromagnetic radiation permits transitions among electronic states

\[ H(t) = - \mu \cdot E(t) \]

where \( \mu \) is the dipole operator and the dot represents the dot product. If the dipole \( \mu \) is aligned with the electric vector \( E(t) \) then \( H(t) = - \mu E(t) \). If they are perpendicular then \( H(t) = 0 \).

\[ \mu = e r \]

where \( e \) is the charge on an electron and \( r \) is the distance.
The time-dependent perturbation has the form of an time-varying electric field

\[ E(t) = E_0 \cos(\omega t) \]

where \( \omega \) is the angular frequency. The electric field oscillation drives a polarization in an atom or molecule. A polarization is a coherent oscillation between two electronic states. The symmetry of the states must be correct in order for the polarization to be created.

The orientation average and time average over the square of the field is \([-\mu \cdot E(t)]^2 \) is \( \mu^2 E_0^2/6 \).
Absorption of visible or ultraviolet radiation leads to electronic transitions.
Absorption of visible or ultraviolet radiation leads to electronic transitions

The change in nodal structure also implies a change in orbital angular momentum.
The interaction of electromagnetic radiation with a transition moment

The electromagnetic wave has an angular momentum of 1. Therefore, an atom or molecule must have a change of 1 in its orbital angular momentum to conserve this quantity. This can be seen for hydrogen atom:

\[ l = 0 \quad \rightarrow \quad l = 1 \]

Electric vector of radiation
The Fermi Golden Rule for optical electronic transitions

\[ k_{12} = \frac{\pi \left( e\langle \Psi_1|q|\Psi_2 \rangle \right)^2 E_0^2}{6\hbar^2} \delta(\omega - \omega_{12}) \]

The rate constant is proportional to the square of the matrix element \( e\langle \Psi_1|q|\Psi_2 \rangle \) times a delta function. The delta function is an energy matching function:

\[ \delta(\omega - \omega_{12}) = 1 \text{ if } \omega = \omega_{12} \]
\[ \delta(\omega - \omega_{12}) = 0 \text{ if } \omega \neq \omega_{12}. \]
A propagating wave of electromagnetic radiation of wavelength $\lambda$ has an oscillating electric dipole, $E$ (magnetic dipole not shown).
The oscillating electric dipole, $E$, can *induce* an oscillating dipole in a molecule as the radiation passes through the sample.
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The type of induced oscillating dipole depends on $\lambda$. If $\lambda$ corresponds to a vibrational energy gap, then radiation will be absorbed, and a molecular vibrational transition will result.

$$\Delta E = \frac{hc}{\lambda}$$
The oscillating electric dipole, $E$, can induce an oscillating dipole in a molecule as the radiation passes through the sample. If $\lambda$ corresponds to an electronic energy gap, then radiation will be absorbed, and an electron will be promoted to an unfilled MO.

$\Delta E = \frac{hc}{\lambda}$
The absorption of light by molecules is subject to several selection rules. From a group theory perspective, the basis of these selection rules is that the transition between two states $a$ and $b$ is *electric dipole allowed* if the electric dipole moment matrix element is non-zero, i.e.,

$$
\langle a | \mu | b \rangle = \int_{\infty}^{\psi} \mu \psi_{b} \, d\tau \neq 0
$$

where $\mu = \mu_{x} + \mu_{y} + \mu_{z}$ is the electric dipole moment operator which transforms in the same manner as the p-orbitals.

$$
\psi_{a} \otimes \mu \otimes \psi_{b} = \psi_{a} \otimes (\mu_{x} + \mu_{y} + \mu_{z}) \otimes \psi_{b}, \text{ must contain the totally symmetric irrep}
$$

...or put another way,

$$
\psi_{a} \otimes \psi_{b} \text{ must transform as any one of } \mu_{x}, \mu_{y}, \mu_{z}
$$
Direct Products: The representation of the product of two representations is given by the product of the characters of the two representations.

Verify that under $C_{2v}$ symmetry $A_2 \otimes B_1 = B_2$

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>$C_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_2 \otimes B_1$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

As can be seen above, the characters of $A_2 \otimes B_1$ are those of the $B_2$ irrep.
Verify that $A_2 \otimes B_2 = B_1$, $B_2 \otimes B_1 = A_2$

Also verify that

- the product of any non-degenerate representation with itself is totally symmetric
- the product of any representation with the totally symmetric representation yields the original representation

Note that,

- $A \times B = B$; while $A \times A = B \times B = A$
- $g \times u = u$; while $g \times g = u \times u = g$. 
Light can be depicted as mutually orthogonal oscillating electric and magnetic dipoles. In infrared and electronic absorption spectroscopies, light is said to be absorbed when the oscillating electric field component of light induces an electric dipole in a molecule.

For a hydrogen atom, we can view the electromagnetic radiation as mixing the 1s and 2p orbitals transiently.
Is the orbital transition $d_{yz} \rightarrow p_x$ electric dipole allowed in $C_{2v}$ symmetry?

None of the three components contains the $a_1$ representation, so this transition is electric dipole forbidden.

A transition between two non-degenerate states will be allowed only if the direct product of the two state symmetries is the same irrep as one of the components of the electric dipole.
How about an \(a_1 \rightarrow b_2\) orbital transition?

\[
\begin{pmatrix} b_2 \\ a_1 \end{pmatrix} \otimes \begin{pmatrix} a_2 \\ b_1 \end{pmatrix} \otimes a_1 = \begin{pmatrix} a_2 \\ a_1 \\ b_2 \end{pmatrix} \otimes a_1 = \begin{pmatrix} a_2 \\ a_1 \\ b_2 \end{pmatrix}
\]

Since \(m_y\) makes the transition allowed, the transition is said to be "y-allowed" or "y-polarized"

Remember the shortcut: \(a_1 \otimes b_2 = b_2\) which transforms as \(\mu_y\)

**Problem** Indicate whether each of the following metal localized transitions is electric dipole allowed in \(\text{PtCl}_4^{2-}\).

(a) \(d_{xy} \rightarrow p_z\)  
(b) \(d_{yz} \rightarrow d_{z^2}\)  
(c) \(d_{x^2-y^2} \rightarrow p_x, p_y\)  
(d) \(p_z \rightarrow s\)