Quantum Mechanical Operators and Wavefunctions

"well behaved" functions (φ), have the following properties

- must be continuous (no "breaks")
- must have continuous derivatives (no "kinks")
- must be normalizable. Mathematically, this means ("dτ" implies integration over all space):

\[ \int \phi^* \phi \, d\tau = C, \quad (C \text{ is a finite constant}). \]

if we multiply \( \phi \) by \( 1/\sqrt{C} \),

\[ \int \left( \frac{\phi^*}{\sqrt{C}} \right) \left( \frac{\phi}{\sqrt{C}} \right) \, d\tau = 1, \quad \frac{\phi}{\sqrt{C}} \text{ is said to be "normalized"} \]

Orthogonality of Wavefunctions

- Two functions, \( \phi \) and \( \chi \), are orthogonal if

\[ \int \phi^* \chi \, d\tau = 0 \]

- Eigenfunctions of QM operators are orthogonal (proof - handout). If 2 or more eigenfunctions (eg., \( \phi_1 \) & \( \phi_2 \)) have the same eigenvalue, then orthogonal eigenfunctions can be “made”:

\[ \chi_1 = \phi_1 \text{ and } \chi_2 = \phi_2 + c\phi_1 \]

where \( c = -\int \phi_1^* \phi_2 \, d\tau / \int \phi_1^* \phi_1 \, d\tau \).

Commuting Operators have Common Eigenfunctions

- This is shown on your handout
- Symmetry operators can’t change the energy of wavefunctions after they “operate”. Symmetry operators therefore commute with the Hamiltonian (\( H \)).
- A set of commuting operators including \( H \) and the symmetry operators \( A, B, \ldots \) have common eigenfunctions.

Example: The H-Atom (Digression)

\[ \mathcal{H} \psi_{\text{nlm}}(r, \theta, \phi) = E_{\text{nlm}} \psi_{\text{nlm}}(r, \theta, \phi) \]

\[ \mathcal{H} = \mathcal{T} + \mathcal{V}(r) = -\frac{\hbar^2}{2m} \nabla^2 - \frac{Ze^2}{r} \]

\[ = -\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \right) + \frac{1}{2mr^2} \mathcal{L}^2 - \frac{Ze^2}{r} \]

where \( \mathcal{L}^2 \) is the (squared) angular momentum operator:

\[ \mathcal{L}^2 = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right) + \frac{\mathcal{L}^2}{\sin^2 \theta} \]

\( \mathcal{L}^2 \) operates only on \( \theta \) and \( \phi \) \( \Rightarrow \) commutes with \( \mathcal{H} \)

\( \frac{\partial}{\partial \theta} \) operates only on \( \theta \) \( \Rightarrow \) commutes with \( \mathcal{H} \) and \( \mathcal{L}^2 \)

Since \( \mathcal{H} \) does not operate on spin variables \( \Rightarrow \)

\( \mathcal{L}^2 \) and \( \mathcal{S}^2 \) also commute with \( \mathcal{H}, \mathcal{L}^2 \), and \( \mathcal{L} \).
Commuting Operators have Common Eigenfunctions

For the hydrogen atom, operators that commute with $\mathcal{H}$ are $L^2$, $L_z$, $S^2$, and $S_z$.

Therefore, the eigenfunctions of $\mathcal{H}$ are also eigenfunctions of $L^2$, $L_z$, $S^2$, and $S_z$.

$L^2$: $l = 0, 1, \ldots, n-1$

$L_z$: $m_l = -l, -l+1, \ldots, l-1, l$ (2$l+1$ values)

$S^2$: ($s = \frac{1}{2}$ for one electron)

$S_z$: ($m_s = -\frac{1}{2}, +\frac{1}{2}$ for one electron, 2$S+1$ values in general)

Group Theory & Quantum Mechanics

Symmetry Operators commute with the molecular electronic or vibrational Hamiltonian:

\[ [R, \mathcal{H}] = RH - HR = 0 \quad \text{or} \quad RH = HR \]

\[ \mathcal{H}\psi_i = \varepsilon_i\psi_i \]

where $\{\varepsilon_i\}$ and $\{\psi_i\}$ are sets of energies and wavefunctions for that Hamiltonian

Group Theory & QM, cont.

Nondegenerate case: only one wavefunction has energy $\varepsilon_i$. Then,

\[ \mathcal{H}R\psi_i = RH\psi_i \]

\[ \mathcal{H}(R\psi_i) = R\varepsilon_i\psi_i = \varepsilon_i(R\psi_i) \]

$R\psi_i$ is a wavefunction with the same energy. Therefore, $R\psi_i = C\psi_i$, where $C$ is a constant with a magnitude of 1 (usually $C = \pm 1$, but it could be complex, $C = e^{i\alpha}$, where $\alpha$ is const.)

Example: Valence MOs of Water

$H_2O$ has $C_{2v}$ symmetry.

The symmetry operators of the $C_{2v}$ group all commute with each other (each is in its own class).

The eigenfunctions of $\mathcal{H}$ must also be eigenfunctions of the symmetry operators $E, C_2, \sigma_v, \sigma_{v'}$.
Building a MO diagram for H$_2$O

$a_1$ orbital of H$_2$O

$b_1$ orbital of H$_2$O

$b_1$ orbital of H$_2$O, cont.
Group Theory & QM, cont.

- Degenerate case: more than one wavefunction has energy $\varepsilon_i$. We still write

$$\mathcal{H}R\psi_i = R\mathcal{H}\psi_i$$

$$\mathcal{H}(R\psi_i) = R\varepsilon_i\psi_i = \varepsilon_i(R\psi_i)$$

Again, $R\psi_i$ is a wavefunction with the same energy, but it is possible that $R\psi_i = \sum_j c_j \psi_j$ where the sum is over all wavefunctions with the same energy ($\varepsilon_i = \varepsilon_j$) — for molecules the degeneracy is usually only 2- or 3-fold.

Higher Dimensional Representations and Degeneracy

- $k$-fold degenerate wavefunctions form a basis for a $k$-dimensional irreducible rep.

- Example: For a molecule with octahedral ($O_h$) symmetry three $p$ orbitals ($p_x$, $p_y$, $p_z$) on the central atom must be degenerate, $\varepsilon_x = \varepsilon_y = \varepsilon_z$.

Demonstrate that the $p$ orbitals form a basis for the $T_{1u}$ representation in $O_h$ symmetry.

- The converse is true: If $k$ wavefunctions are degenerate, they form a basis for a $k$-dimensional irreducible representation.
The Direct Product - What is it for?

It is often important to know whether integrals involving bases of IRs are zero, i.e., if $f$ and $g$ are basis functions belonging to $\Gamma_1$ and $\Gamma_2$:

$$\int_{\text{all space}} fg \, d\tau = 0$$

If the integrand, $fg$, belongs to the totally symmetric IR, then this is nonzero. Otherwise it is identically zero.

States and Configurations

Each of the electronic states of an atom or a molecule are usually described as being built up from one (or perhaps more than one) configuration. Similarly, the total vibrational state of a molecule derives from a description of which individual modes are excited.

Atomic Example: What states arise from a $1s^2 \, 2s^2 \, 2p^2$ (C atom ground) configuration?


Carbon: Atomic Energy Levels

Experimental atomic energy levels are shown, with energies in cm$^{-1}$.

http://physics.nist.gov/PhysRefData/ASD/index.html
The Direct Product - What is it?

- We often seek to know the symmetries of electronic states that arise from configuration with partially filled orbital subshells. For example, what states arise from \((t_{2g})^1 (e_g)^1\) configuration for a \(d^2\) octahedral complex?

\[ \uparrow \quad \text{e}_g \]

\[ \uparrow \quad \text{t}_{2g} \]

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Illustration: $S_3$ Operation in $D_{3h}$

$E'$ representation; $x$ and $y$ basis. $S_3$ matrix:
\[
\begin{bmatrix}
-1/2 & \sqrt{3}/2 \\
\sqrt{3}/2 & -1/2
\end{bmatrix}
\]

$A_2^\prime$ representation; $z$ basis. $S_3$ "matrix": $-1$

Direct Product rep.; $xz$ and $yz$ basis.
$S_3$ matrix:
\[
\begin{bmatrix}
1/2 & -\sqrt{3}/2 \\
\sqrt{3}/2 & 1/2
\end{bmatrix}
\]

Properties and Uses of Direct Products

- The direct product representation $\Gamma_{AB'}$ obtained from $\Gamma_A$ and $\Gamma_B$, will only contain the totally symmetric representation if $\Gamma_A$ and $\Gamma_B$ belong to the same IR.

Illustration: $S_3$ Operation in $D_{3h}$

$E'$ rep.; $p_x$ and $p_y$ basis. $S_3$ matrix:
\[
\begin{bmatrix}
-1/2 & -\sqrt{3}/2 \\
\sqrt{3}/2 & -1/2
\end{bmatrix}
\]

$E''$ rep.; $d_{xz}$ and $d_{yz}$ basis. $S_3$ matrix:
\[
\begin{bmatrix}
1/2 & \sqrt{3}/2 \\
-\sqrt{3}/2 & 1/2
\end{bmatrix}
\]

Direct Product rep.; $p_xd_{xz}, p_xd_{yz}, p_yd_{xz}, p_yd_{yz}$ basis.
$S_3$ matrix:
\[
\begin{bmatrix}
-1/4 & -\sqrt{3}/4 & -\sqrt{3}/4 & -3/4 \\
\sqrt{3}/4 & 1/4 & 3/4 & -\sqrt{3}/4 \\
\sqrt{3}/4 & 3/4 & 1/4 & -\sqrt{3}/4 \\
-3/4 & \sqrt{3}/4 & \sqrt{3}/4 & 1/4
\end{bmatrix}
\]

Proof

The number of times the $i^{th}$ IR is contained in $\Gamma_{AB}$ is
\[
a_i = \frac{1}{\hbar} \sum_{R} \chi_{AB}(R)\chi_i(R)
\]

$\chi_1(R) = 1$ for all $R$ \Rightarrow $a_i = \frac{1}{\hbar} \sum_{R} \chi_{AB}(R)$

but we know that $\chi_{AB}(R) = \chi_A(R)\chi_B(R)$, so
\[
a_i = \frac{1}{\hbar} \sum_{R} \chi_A(R)\chi_B(R) = \delta_{AB}
\]

where the final equality arises from orthogonality.
**SPECTRAL TRANSITION PROBABILITIES**

When are electronic transitions allowed?

For example, is the $^2T_{2g} \rightarrow ^2E_g$ transition illustrated below “symmetry allowed”?

\[ \begin{array}{c}
\text{--- e}_g \\
\text{--- t}_{2g} \\
\end{array} \rightarrow \begin{array}{c}
\text{--- e}_g \\
\text{--- t}_{2g} \\
\end{array} \]

\[ ^2T_{2g} \rightarrow ^2E_g \]

---

**TRANSITION ENERGIES**

The energetic restriction on the allowedness of optical transitions like the $^2T_{2g} \rightarrow ^2E_g$ transition illustrated earlier is familiar:

\[ E_f - E_i = h\nu \]

But this doesn’t deal with symmetry.

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**Transition Probabilities, Symmetry Aspects**

I $\propto$ transition moment:  

\[ I \propto \int \psi_i \mu \psi_j d\tau \]

\[ \mu = \sum_i q_i x_i + \sum_i q_i y_i + \sum_i q_i z_i \]

$\mu$ is the dipole moment operator

\[ I_x \propto \int \psi_i x \psi_j d\tau \]

\[ I_y \propto \int \psi_i y \psi_j d\tau \]

\[ I_z \propto \int \psi_i z \psi_j d\tau \]

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**Transition Probabilities, Symmetry Rules**

An electric dipole transition will be allowed with $x$, $y$, or $z$ polarization if the direct product of the representations of the two states concerned is or contains the irreducible representation to which $x$, $y$, or $z$, respectively, belongs.

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See Harris & Bertolucci, pp. 130-5.
Summary

- In the handout, “Transitions Between Stationary States (Adapted from Harris and Bertolucci, p. 130)”, an expression for the probability that a system in its ground state, ψ₀, can be stimulated by radiation into an excited state, ψ₁, is derived:

\[ \Psi(\mathbf{r},t) = c₀(t)\Psi₀(\mathbf{r},t) + c₁(t)\Psi₁(\mathbf{r},t) \]

\[ \frac{dc₁}{dt} = \xi(t)c₀(\mathbf{r},t) \left(\mu_0^2 + \mu_1^2 + \mu_2^2\right) \]

assuming \( c₀(0) = 1 \) and \( c₁(0) = 0 \), where \( \xi(t) \) is proportional to the light intensity and \( \mu_{ij} \) are the transition moment integrals.

- This expression applies to an integral over all wavelengths of incident light (in the dipole approximation) and was the form used to evaluate whether an electron transition was symmetry allowed.

Allowedness

- In group theory, prescription for deciding whether a transition is dipole-allowed is straightforward:
  - If the ground and excited states respectively belong to the \( \Gamma₀ \) and \( \Gamma₁ \) representations of the point group of the molecule in question, then a transition is dipole-allowed if and only if
    \[ \Gamma₀ \otimes \Gamma₁ \text{ contains } \Gamma₃ \]
    - for \( x \)-polarized light
    - for \( y \)-polarized light
    - for \( z \)-polarized light
  - Spin doesn’t change: \( \Delta S = 0 \). For states where large spin-orbit mixing is possible (large \( \zeta \) and/or small \( \Delta \) between mixed states), the rule is weakened.

Examples

- Is the \( ^2\text{T}_{2g} \rightarrow ^2\text{E}_g \) transition illustrated earlier “symmetry allowed”?
- What about a \( ^2\text{E} \rightarrow ^2\text{T}_2 \) transition for a tetrahedral complex?

\[ ^2\text{E} \quad ^2\text{T}_2 \]

\[ \begin{array}{c}
\uparrow \quad \downarrow \\
\downarrow \quad \uparrow \\
\end{array} \]

\[ t₂ \quad t₂ \]

\[ e \quad e \]

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Types of Transitions: d-d

a) intramolecular e⁻ transfer within the d-orbital manifold

b) Values for ε vary: up to 1,000 M⁻¹ cm⁻¹ (moderately intense) for spin-allowed transitions in non-centrosymmetric molecules; ~10 M⁻¹ cm⁻¹ for spin-allowed transitions in centrosymmetric molecules (weak); ~10⁻¹ M⁻¹ cm⁻¹ for spin-forbidden transitions in centrosymmetric molecules (very weak).

c) 1-e⁻ transitions much more intense (2-e⁻ transitions typically 10⁻² times weaker)

d) Shoulders and/or broad peaks expected where Jahn-Teller distortions apply.

Identifying Nonzero Matrix Elements

Molecular Orbitals, ψ_μ (μ = 1, 2, …), for molecules are usually expanded in terms of basis functions: (ψ_μ = c_1μφ_1 + c_2μφ_2 + …)

These basis functions, {φ_1, φ_2, …}, may be atomic orbitals, or as we shall see, they may be Symmetry Adapted Linear Combinations (SALCs) of atomic orbitals. We shall see that it is important to be able to identify whether integrals (called matrix elements) of the form below are zero by symmetry.

H_{ij} ≡ \int \phi_i \mathbf{H} \phi_j \, d\tau = 0

SALCs are constructed so that they form basis functions for the IRs of the system (molecule or crystal).

Hamiltonian Matrix Elements, H_{ijr}

involving SALCs are nonzero only if φ_i and φ_j belong to the same IR.