

CHEM400/740: Quantum Mechanics in Chemistry

Chapter#02

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1. Review Session

The full electronic Hamiltonian:

$$\hat{H} = \hat{h} + \hat{V} \quad (1)$$

- The two-electron operator:

$$\hat{V} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \quad (2)$$

- The one-electron operator:

$$\hat{h} = \sum_i \hat{h}(i) \quad (3)$$

NOTE: sum over all electrons.

- The individual one-electron operator includes kinetic energy and potential energy of nuclei and electrons:

$$\hat{h}(1) = -\frac{1}{2} \nabla_1^2 + v_{(1)}^{\text{Ne}} \quad (4)$$

Solve the one-electron Schrödinger equation:

$$\hat{h}(1)\psi_a(1) = \varepsilon_a\psi_a(1) \quad (5)$$

NOTE:

$a = 1, 2, 3, \dots, M$ (finite in 'finite basis')

Add spin: $\psi_c(r_1)\alpha \rightarrow \psi_c(1)$.

$\psi_c(r_1)\beta \rightarrow \bar{\psi}_c(1)$.

Any product function:

$$\psi_\lambda = \prod_{k \in \lambda} \psi_{a_i}(r_i) \sigma_k \quad (6)$$

NOTE:

λ indicates a configuration of the orbitals that are occupied.

σ_k includes spin up, α , and spin down, β .

Each of the product, ψ_λ , is the eigenfunction of Hamiltonian with eigenvalue, $\sum_{i \in \lambda} \varepsilon_{a_i}$.

Antisymmetry requirement:

$$|\phi_\lambda\rangle = \hat{A}\psi_\lambda \quad (7)$$

$$\hat{A} = \sum_k^{N!} (-1)^{p_k} \hat{P}_k \quad (8)$$

NOTE:

\hat{A} represents antisymmetrization operator.

p_i is called the parity of the permutation (0 or 1).

$N!$ is the total number of permutation of N electrons.

(+) sign: even number of interchanges

(-) sign: odd number of interchanges.

Or use Slater determinants:

$$|\phi_\lambda\rangle = |\psi_a(1)\psi_b(2)\cdots\bar{\psi}_i\cdots\bar{\psi}_Z(N)| \quad (9)$$

a) interchange of electron-label.

b) interchange of spin-orbitals.

\implies The easiest way to label about spin.

These are building blocks of electronic structure theory!

2. Full Configuration Interaction

2.1 Orders of the orbitals

Rewrite the eigenfunction of Hamiltonian:

$$\hat{H}\psi = E\psi \quad (10)$$

Multiply by the phase factor, a complex number:

$$\hat{H}e^{i\psi}\psi = Ee^{i\psi}\psi \quad (11)$$

NOTE:

$e^{i\psi}\psi$ is also the eigenstate.

$e^{i\psi}$: arbitrary phase.

even scaling factor \implies change norm of the wavefunction, ψ .

We can order the orbitals, as changing the order in a determinant introduces a sign at most. In-

cluding spin, we might also say:

$$|\phi_\lambda\rangle = |\psi_a(1)\psi_b(2)\cdots\psi_Z(N_\alpha)\bar{\psi}_{a'}(1)\bar{\psi}_{b'}(2)\cdots\bar{\psi}_Z(N_\beta)\rangle \quad (12)$$

NOTE:

First includes N_α electrons with α orbitals, then N_β electrons with β orbitals.

- If we have M spatial orbitals, the number of distinct determinants with N_α, N_β is $\binom{M}{N_\alpha}, \binom{M}{N_\beta}$. The number of determinants is gigantic. Each of these determinants is eigenstate of $\hat{h} = \sum_i \hat{h}(i)$ with energy, $\sum_i \varepsilon_i$. Also, eigenstates of $\hat{s}_Z = \frac{1}{2}(N_\alpha - N_\beta)$. One has to use correct orbitals!
- If the orbitals are chosen to be orthonormal, these states are orthogonal. To normalize one has to introduce a factor $\frac{1}{\sqrt{N!}}$. (proof later)
 - 1) Orthonormality of orbitals:

$$\langle\psi_a|\psi_b\rangle = \int \psi_a^*(\vec{r})\psi_b(\vec{r})d^3r = \delta_{\alpha\beta} \quad (13)$$

NOTE:

$\int \psi_a^*(\vec{r})\psi_b(\vec{r})d^3r$ is called overlap integral.

- 2) Non-orthonormality of orbitals:

$$\langle\psi_a|\bar{\psi}_b\rangle = \langle\psi_a\alpha|\psi_b\beta\rangle = \langle\psi_a|\psi_b\rangle_{\text{spatial}} \underbrace{\langle\alpha|\beta\rangle}_0 = 0 \quad (14)$$

NOTE:

Orbitals with different spin are always orthogonal. $\implies \langle\alpha|\beta\rangle = 0$.

- 3) If orbitals satisfy $\hat{h}(1)\psi_a(1) = \varepsilon_a\psi_a(1)$ and $\varepsilon_a \neq \varepsilon_b$, we can get the overlap of the eigenfunctions, $\langle\psi_a|\psi_b\rangle = 0$, where $\hat{h}(1)$ is the Hermitian operator.
- 4) If orbitals satisfy $\hat{h}(1)\psi_a(1) = \varepsilon_a\psi_a(1)$ and $\varepsilon_a = \varepsilon_b$, we can always make such orbitals orthogonal/ orthonormal, $\langle\psi_a|\psi_b\rangle = \delta_{ab}$, where $\hat{h}(1)$ is the Hermitian operator.

Proof:

$$\begin{aligned} \hat{h}(c_1\psi_a + c_2\psi_b) \\ &= c_1\varepsilon_a\psi_a + c_2\varepsilon_b\psi_b \\ &= \varepsilon_a(c_1\psi_a + c_2\psi_b) \end{aligned} \quad (15)$$

Any linear combination of degenerate orbitals is also eigenstate.

\implies Use this to create orthonormal set.

$$\text{In general, } \langle\psi_a|\psi_b\rangle = \delta_{ab} = \begin{cases} 1 & a = b \\ 0 & \text{otherwise} \end{cases}$$

- The determinants, $|\phi_\lambda\rangle = \frac{1}{\sqrt{N!}} \hat{A}(\psi_a(1) \cdots \psi_Z(N))$, use orthonormal basis for Hilbert space. In many-electron system, creating the orthonormal basis is convenient to consider and calculate, hence $\langle \phi_\lambda | \phi_\mu \rangle = \delta_{\lambda\mu}$.

2.2 Two-electron Interaction

Inclusion of electron repulsion in Hamiltonian:

$$\hat{V} = \frac{1}{2} \sum_{i \neq j} \frac{1}{r_{ij}} \quad (16)$$

Application of the linear variation principal: the full configuration interaction(CI) model of quantum chemistry.

The eigenstates of one-electron Hamiltonian can be used as a basis to set expansion functions for the true many-electron problem. Then, we can make linear combination:

$$|\psi\rangle = \sum_{\lambda} c_{\lambda} |\phi_{\lambda}\rangle \quad (17)$$

NOTE:

The c_{λ} are coefficients to be determined.

The $|\phi_{\lambda}\rangle$ form an in principal complete basis.

To obtain the coefficients we can apply variational principal. We need to get the expectation value of the Hamiltonian (energy) and minimize the energy.

$$\frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle} = \langle H \rangle = E \quad (18)$$

This leads to a matrix eigenvalue problem. More details see Materials: “Modern Quantum Chemistry” Chapter#1 (Szabo and Ostlund).

$$\sum_{\mu} \langle \phi_{\lambda} | \hat{H} | \phi_{\mu} \rangle c_{\mu} = E c_{\lambda} \quad (19)$$

$$HC = CE \quad (20)$$

- The orthonormal basis has no overlap matrix.
- The Equation (20) is the Heisenberg version of Quantum Mechanics. This is also called “matrix-mechanics”.
- Compared with the Schrödinger equation, $\hat{H}\psi = E\psi$, both equations are equivalent and need to solve matrix eigenvalue problem. The Schrödinger equation is called “wave-mechanics”.
- In actual research, we never use Schrödinger equation. The research always uses matrix-eigenvalue equations to calculate by computers. This becomes a nice problem in linear algebra.

This presents the best solution within the basis set.

2.3 Excited Determinants and Full Configuration Interaction

If we assume we have M orbitals of both α spin and β spin. This is determined by basis set used to expand orbitals.

$$\begin{aligned} M & \quad \text{spatial orbitals} \\ N_\alpha & \quad \alpha \text{ electrons} \\ N_\beta & \quad \beta \text{ electrons} \\ (N_\alpha - N_\beta) &= 2\langle S_Z \rangle \end{aligned} \tag{21}$$

The number of determinants / the number of coefficients:

$$\binom{M}{N_\alpha} \cdot \binom{M}{N_\beta}$$

- Choose N_α α -orbitals out of M .
- Choose N_β β -orbitals out of M .

Example for ethylene:

$$M \approx 100$$

$$N_\alpha \approx 10 = N_\beta$$

$$\binom{100}{10} = \frac{100 \cdot 99 \cdots 91}{10 \cdot 9 \cdots 1} \approx \left(\frac{100}{10}\right)^{10} = 10^{10}$$

$$\text{The number of determinants} = 10^{10} \times 10^{10} = 10^{20}$$

$$\text{The number of matrix-elements} = \langle \phi_\lambda | \hat{H} | \phi_\mu \rangle \approx 10^{20} \cdot 10^{20} = 10^{40}$$

Absolutely impossible to store Hamiltonian matrix, let alone diagonalize. Even to store solution, c_μ , is impractical / impossible.

This is called full CI solution, such calculations are done for small molecules or small basis sets.

- FCI: In principle, the full CI is exact solution in complete one-particle basis
 - Exact solution in finite / small basis set. \implies A rigorous benchmark to compare against.
 - Conceptually simple. Insight in solutions to S.E.
 - Only requires $\langle \phi_\lambda | \hat{H} | \phi_\mu \rangle$. Rest in linear algebra can be used in computer science.
- CAS-CI: Take small set of 'active' orbitals and 'active' electrons. Next, do Full CI for subproblem. Combine CAS-CI with other methods, like: DFT, perturbation theory, and coupled cluster. These methods can be excellent for very hard problems.

It is evident one needs to make approximations. We will see how to do this without losing accuracy (much).

3. Hartree-Fock Approximation

This is a cornerstone of most wave function based on electronic structure approaches. $|\psi_{HF}\rangle$ is approximated by a single determinant, $|\phi\rangle$. Choose the orbitals $\psi_a, \psi_b, \dots, \psi_Z$.

$$|\phi\rangle = \frac{1}{\sqrt{N!}} |\psi_a(1)\psi_b(2)\cdots\psi_Z(N)| \quad (22)$$

The orbitals are optimized such that the energy is minimized. Hence, the energy for full Hamiltonian, $\langle\phi|\hat{H}|\phi\rangle$ is minimum. We do not solve for one electron, like $\hat{h}\psi_a = \epsilon_a\psi_a$, because they do not take into account the repulsion between electrons and electrons, \hat{V}_{ee} . Also, orbitals are orthonormal, $\langle\psi_a|\psi_b\rangle = \delta_{ab}$.

I will briefly state the equations of Hartree-Fock approximation, we will discuss in more details later.

Firstly, expand the molecular orbitals in basis set and introduce a finite atomic basis set, $|\chi_\mu\rangle$. We might choose basis set 6-31g(d,p) or cc-pvtz in Gaussian as an input to do some calculations (fixed by nuclear configurations).

$$\psi_a(1) = \sum_{\mu} \chi_{\mu}(1) c_{\mu a} \quad (23)$$

Molecular orbitals are linear combinations of atomic orbitals.

Here are some important quantities in AO-basis we can calculate:

- Overlap integral:

$$\langle\chi_{\mu}|\chi_{\nu}\rangle = S_{\mu\nu} \quad (24)$$

- One-electron integrals:

$$\langle\chi_{\mu}|\hat{h}|\chi_{\nu}\rangle = \hat{h}_{\mu\nu} = \int \chi_{\mu}^*(1) \hat{h}(1) \chi_{\nu}(1) d1 \quad (25)$$

- Two-electron integrals:

$$\langle\chi_{\mu}\chi_{\nu}|\frac{1}{r_{12}}|\chi_{\lambda}\chi_{\sigma}\rangle \equiv \langle\mu\nu|\lambda\sigma\rangle = \int \chi_{\mu}^*(1) \chi_{\nu}^*(2) \frac{1}{r_{12}} \chi_{\lambda}(1) \chi_{\sigma}(2) d1d2 \quad (26)$$

NOTE:

χ_{μ} indicates spin-orbital here.

We can also use round brackets to describe two-electron integral, $(\mu\lambda|\nu\sigma)$. They are same integral.

$$\underbrace{(\mu\lambda|\nu\sigma)}_{(11|22)} = \underbrace{\langle\mu\nu|\lambda\sigma\rangle}_{\langle 12|21\rangle} \quad (27)$$

- Anti-symmetrized two-electron integrals:

$$\langle \mu\nu || \lambda\sigma \rangle = \langle \mu\nu | \lambda\sigma \rangle - \langle \mu\nu | \sigma\lambda \rangle \quad (28)$$

These AO-integrals are calculated at the start of a calculation.

A Hartree-Fock calculation follows Self-consistent procedure.

3.1 Self-consistent Procedure

Assume a guess for molecular orbitals, the molecular coefficient, $C_{\mu i}$ ($i = 1, N$ and $\mu = 1, N$).

- 1) Calculate density matrix for occupied orbitals:

$$D_{\mu\nu} = \sum_{i=1,N} C_{\mu i} C_{\nu i} \quad (29)$$

- 2) Calculate Fock-matrix:

$$F_{\mu\nu} = \hat{h}_{\mu\nu} + \sum_{\lambda\sigma} \langle \mu\lambda || \nu\sigma \rangle D_{\lambda\sigma} \quad (30)$$

- 3) Solve (generalized) eigenvalue problem:

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\lambda} S_{\mu\lambda} C_{\lambda i} \varepsilon_i \quad (31)$$

\Rightarrow Molecular orbitals $C_{\nu i}$, Orbital energies ε_i

If new orbitals ($C_{\nu i}$) from step 3) agree with input orbitals ($C_{\mu i}$), they are converged. The converged result is the correct HF solution.

Otherwise go back to step 1). Iterate until F, D, C no longer change.

This is called a self-consistent filled procedure.

At self consistency, $D^{(\text{in})} \rightarrow F \rightarrow \text{Diagonalize} \rightarrow D^{(\text{out})}$. When $D^{(\text{in})} = D^{(\text{out})}$, the energy of determinant is optimal (stationary).

In practice one uses smart converge techniques. HF calculations are cumbersome sometimes.

NOTE (More discussion later):

- The determinant in HF is unique (up to a phase).
- The density matrix is unique (given the basis set).
- Molecular orbitals are not unique.

$$\sum_i C_{\mu i}^* C_{\nu i} = D_{\mu\nu} \quad (32)$$

One can rotate occupied orbitals.

$$\sum_i C'_{\mu i} = C_{\mu j} u_{ji} \quad (33)$$

Note that the u_{ji} is unitary.

Hartree-Fock in practice:

- Decent results for geometry optimization (small basis set).
- Reasonable harmonic frequencies.
- Very poor for thermo chemistry, energy differences.
- Not good for potential energy surface.

However, total energies in HF are remarkably accurate.

$$E_{\text{HF}} \gtrsim 99.5\% \text{ of } E_{\text{FCI}} \quad (34)$$

Total energies are huge. For this reason HF by itself is not good enough. One needs to go beyond: inclusion of electron correlation. Also, HF calculation is often the starting point.

4. Symmetry in Quantum Mechanics

This is a vast topic. I wish to discuss have the general principles. I will not go into full detail. In a next section, I will discuss the permutation group, angular momentum and spin.

4.1 General Principle of Symmetry

Suppose that we know the solutions to the S.E.

$$\hat{H}|\phi_n\rangle = E_n|\phi_n\rangle \quad (35)$$

$$\langle\phi_n|\phi_m\rangle = \delta_{nm} \quad (36)$$

These solutions form an orthonormal basis for the Hilbert space.

Question:

Can I find operators \hat{u} such that $\hat{u}|\phi_n\rangle$ also form an orthonormal basis, while having the same energies E_n ?

$$(|\phi_m\rangle)^\dagger = \langle\phi_m| \quad \hat{u}^\dagger \hat{u} = 1 \quad (37)$$

$$(\hat{u}|\phi_m\rangle)^\dagger \hat{u}|\phi_n\rangle = \langle\phi_m|\hat{u}^\dagger \hat{u}|\phi_n\rangle = \delta_{mn} \quad (38)$$

$$\hat{H}\hat{u}|\phi_n\rangle = E_n\hat{u}|\phi_n\rangle \quad (39)$$

NOTE:

- 1) The orthonormal condition implies:

$$\langle \phi_m | \hat{u}^\dagger \hat{u} | \phi_n \rangle = \langle \phi_m | \phi_n \rangle \quad (40)$$

\hat{u} is a unitary operator: $\hat{u}^\dagger \hat{u} = 1$ and $\hat{u}^\dagger = \hat{u}^{-1}$. Note that the unitary operators preserve orthonormality of a basis, which means $\hat{u}^\dagger \neq \hat{u}$ in general and $\hat{u}^{-1} \neq \hat{u}$ in general.

Reflection in a plane is its own inverse.

Unitary in linear algebra preserves angles and length of a set of vector when general rotation.

In physics some symmetries are anti-unitary (time-reversal) then $\langle u\phi | u\psi \rangle = \langle \phi | \psi \rangle^*$ This is not our usual inner product.

- 2) \hat{u} commutes with \hat{H} .

$$\begin{aligned} \hat{H}(\hat{u}|\phi_n\rangle) &= (\hat{u}|\phi_n\rangle)E_n \\ &= \hat{u}\hat{H}|\phi_n\rangle \quad \forall \phi_n \end{aligned} \quad (41)$$

$$\hat{H}\hat{u} = \hat{u}\hat{H} \quad (42)$$

$$[\hat{H}, \hat{u}] = 0 \quad (43)$$

This is true for all $|\phi_n\rangle$.

- 3) If \hat{u} commutes with \hat{H} , then also $\hat{u}^\dagger = \hat{u}^{-1}$.

$$\hat{H}\hat{u} = \hat{u}\hat{H} \quad (44)$$

$$\hat{u}^{-1}\hat{H}\hat{u} = \hat{u}^{-1}\hat{u}\hat{H} = \hat{H} \quad (45)$$

$$\hat{u}^{-1}\hat{H}(\hat{u}\hat{u}^{-1}) = \hat{H}\hat{u}^{-1} \quad (46)$$

$$\hat{u}^{-1}\hat{H} = \hat{H}\hat{u}^{-1} \quad (47)$$

$$\hat{u}^\dagger \hat{H} = \hat{H}\hat{u}^\dagger \quad (48)$$

- 4) If \hat{u}_1 and \hat{u}_2 commute, and unitary, then also $\hat{u}_1\hat{u}_2$.

$$\text{a) } \hat{H}\hat{u}_1\hat{u}_2 = \hat{u}_1\hat{H}\hat{u}_2 = \hat{u}_1\hat{u}_2\hat{H}$$

$$\text{b) } (\hat{u}_1\hat{u}_2)(\hat{u}_1\hat{u}_2)^\dagger = \hat{u}_1\hat{u}_2\hat{u}_2^\dagger\hat{u}_1^\dagger = \hat{u}_1\hat{u}_1^\dagger = 1$$

NOTE:

$$\hat{u}_1^\dagger\hat{u}_2^\dagger\hat{u}_1\hat{u}_2 \neq 1$$

- 5) Linear operators are associative.

$$\hat{u}_1(\hat{u}_2\hat{u}_3) = (\hat{u}_1\hat{u}_2)\hat{u}_3 = \hat{u}_1\hat{u}_2\hat{u}_3 \quad (49)$$

Always holds for matrix multiplication.

It follows that the (full) set of symmetry operations \hat{u}_i form a mathematical group.

4.2 Group

Definition of a group:

Set elements $\{g_i\}$ form a group iff:

- 1) $g_i g_j \in g$ if g_i and g_j is g .
- 2) $g_i (g_j g_u) = (g_i g_j) g_u = g_i g_j g_u$ (Associative)
- 3) $\hat{I} \in g$, $g_i \cdot \hat{I} = \hat{I} \cdot g_i = g_i$
- 4) $g_i^{-1} \in g$, $g_i^{-1} \cdot g_i = \hat{I}$

The theory of groups \iff The theory of symmetry

More details about Groups (Mathematical):

See Link: [Wikipedia Website Link on Groups \(Mathematical\)](#)

Example of a group(1):

Elements of $z \in \{0, \pm 1, \pm 2, \pm 3\}$.

$g_i \otimes g_j$, \otimes means group multiplication.

$z_i + z_j$

Whole numbers from a group under addition:

$z_1, z_2 \quad z_1 + z_2 \in \mathbb{Z}$

$z_1 + (z_2 + z_3)$ Associative

$\hat{I} = 0 \quad 0 + z_1 = z_1$

$z_1 + (-z_1) = 0 \implies \hat{I}$

Example of a group(2):

Another group: rational numbers, excluding 0 under multiplication.

$x, y \longrightarrow z$ rational

$x(x^{-1}) = 1$, with identity, 1. ($x \cdot 1 = 1 \cdot x = x$)

Why is 0 excluded? $0^{-1} = ?$

4.3 Example of Groups in Physics

Symmetries in physics	Conservation Laws (Noether Theorem)
Translational	Conservation of Linear Momentum
Rotations	Angular Momentum is Conserved
Translation in Time	Conservation of Energy
Rotation of Electron Spin	Conservation of Spin-angular Momentum

- Overall translation, $\vec{x} \longrightarrow \hat{T}_a \vec{x} = \vec{x} + \vec{a}$

$$(\hat{T}_a \psi)(\hat{T}_a x) \equiv \psi(x) \quad (50)$$

NOTE:

$\hat{T}_a\psi$: translated function.

Translated function in translated point has value of original function in original point.

$$\hat{T}_a^{-1}\hat{T}_a\psi(\hat{T}_ax) = \hat{T}_a^{-1}\psi(x) \quad (51)$$

$$\psi(T_ax) = \hat{T}_a^{-1}\psi(x) \quad (52)$$

$$\hat{T}_b = \hat{T}_a^{-1} \quad (53)$$

$$\hat{T}_b\psi(x) = \psi(\hat{T}_b^{-1}x) \quad (54)$$

This is general definition (Equation 54) of operator on a function, if one knows the operation on coordinates.

- Overall Rotation (nuclei + electrons)

$$R\psi(x) = \psi(R^{-1}x) \quad (55)$$

Rotations are associated with angular momentum theory, like $\hat{L}_x, \hat{L}_y, \hat{L}_z, \hat{L}^2$. All of angular momentum theory from commutation relations, $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$.

- Multiplication by a phase

$$|\psi\rangle = e^{i\phi}|\psi\rangle \quad (56)$$

Same phase for every state.

This is origin of gauge theories, electron-magnetism.

- Permutations of electronic coordinates.

$$\hat{P}_\lambda\psi(x_1, x_2, \dots, x_N) = \psi(\hat{P}_\lambda^{-1}(x_1, \dots, x_N)) \quad (57)$$

- Overall rotation of electron spin, for example definition of the z-axis for s_z operator.

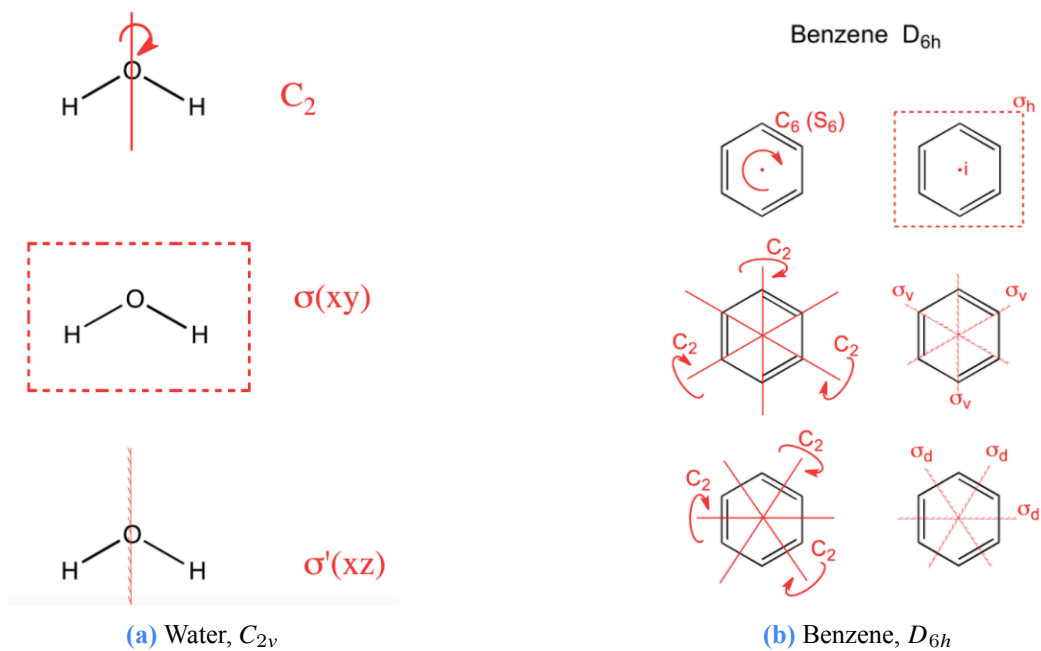
This is the conservation of spin-angular momentum. $\hat{s}_z, \hat{s}_x, \hat{s}_y, \hat{s}^2$ commute with the \hat{H} . We can use them to build a “rotation group” in spin space. Analogy to rotation in space, you need to rotate around 4π to get the identity.

- Point group symmetry in Chemistry. If one rotates nuclei and electrons, Hamiltonian is invariant. Now rotate only electronic part of the wave function. Equivalently rotate nuclei in opposite position.

$$\hat{R}\psi(\vec{r}, Q_\alpha) = \psi(\vec{r}, RQ_\alpha) \quad (58)$$

Hamiltonian is invariant under operations. It means nuclei map onto one another.

Point group of molecule:

**Figure 1** Point Group of Molecules

More details about Groups in Physics:

See Link: [Wikipedia Website Link on Groups in Physics](#)

4.4 Consequences of Symmetry

Summary 4.1

Summary of Symmetry Considerations (Abstract Discussion)

1) Unitary operators preserve orthonormality of a basis.

$$\hat{u}^\dagger \hat{u} = I; \hat{u}^\dagger = \hat{u}^{-1}$$

$$\langle \phi_k | \hat{u}^\dagger \hat{u} | \phi_l \rangle = \langle \phi_k | \phi_l \rangle = \delta_{kl}$$

if original basis is orthonormal.

2) If $[\hat{H}, \hat{u}] = 0$, then if $\hat{H}|\psi\rangle = E|\psi\rangle$.

$$\hat{H}(\hat{u}|\psi\rangle) = E(\hat{u}|\psi\rangle)$$

$\hat{u}|\psi\rangle$ is eigenstate of \hat{H} with the same energy E .

3) If unitary \hat{u}_1, \hat{u}_2 and $[\hat{H}, \hat{u}_i] = 0, i = 1, 2$. Then,

$$\hat{u}_3 = \hat{u}_1 \hat{u}_2$$

a) \hat{u}_3 is a unitary.

b) \hat{u}_3 commutes with \hat{H} .

4) $\hat{u}^\dagger = \hat{u}^{-1}$ is unitary and commutes with \hat{H} .

5) I is unitary and commutes with \hat{H} .

\Rightarrow The set of symmetry operators \hat{u}_i form a mathematical group. (Statement 2-5: postulates that define a mathematical group.)

\Rightarrow All aspects of group theory (a part of algebra) apply to symmetry in Quantum Mechanics.

What if E_n is non-degenerate?

4.4.1 Example: Particle on a Ring

The Schrödinger equation of a particle on a ring:

$$-\frac{\hbar^2}{2mR^2} \frac{d^2\psi(\phi)}{d(\phi)^2} = E\psi(\phi) \quad (59)$$

$$\hat{H} = -\frac{\hbar^2}{2mR^2} \frac{d^2}{d\psi^2} = \frac{\hat{L}_z}{2mR^2} \quad (60)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \psi} \quad (61)$$

$$I = mR^2 \quad (62)$$

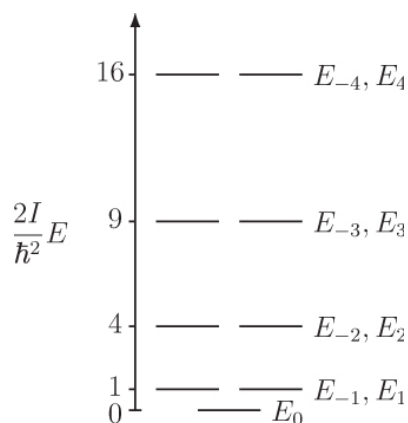


Figure 2 The energy level of a particle on a ring.

The eigenfunctions corresponding to $+m$ and m are linearly independent, so both must be accepted. Therefore all eigenvalues, except E_0 , are two-fold (or doubly) degenerate. The eigenfunctions can all be written in the form $\text{const } e^{ik\phi}$, with m allowed to take either positive and negative values (or 0).

NOTE:

The degeneracy of 2 means that two different wave functions with same eigenvalues.

Different wave functions mean more different than overall phase.

NOT different: $|\phi_n\rangle \longrightarrow (e^{ik\phi})|\phi_n\rangle$ is also eigenstate.

Degenerate states: choose the orthonormal.

General solution:

$$f(\phi) = c_1 e^{ik\phi} + c_2 e^{-ik\phi} \quad (63)$$

Solutions are not unique. Consider:

$$\begin{cases} \sin(k\phi) \\ \cos(k\phi) \end{cases} \quad \text{or} \quad \begin{cases} e^{ik\phi} \\ e^{-ik\phi} \end{cases}$$

$$\cos(k\phi) = \frac{1}{2}(e^{ik\phi} + e^{-ik\phi}) \quad (64)$$

$$\sin(k\phi) = \frac{1}{2}(e^{ik\phi} - e^{-ik\phi}) \quad (65)$$

The set of solutions / the subspace of solutions that we choose is unique.

Summary 4.2

The solution of a particle on a ring:

$\frac{1}{\sqrt{2\pi}}e^{ik\phi}$ and $\frac{1}{\sqrt{2\pi}}e^{-ik\phi}$ are eigenstates of \hat{H} with the same eigenvalue (energy), $\frac{k^2\hbar^2}{2mR^2}$ ($\frac{k^2\hbar^2}{2I}$).
Freedom in choice according to different basis sets or different subspaces:

a) Real eigenfunctions:

$$\begin{cases} \frac{1}{\sqrt{\pi}}\sin(k\phi) \\ \frac{1}{\sqrt{\pi}}\cos(k\phi) \end{cases} \quad k=0 : \frac{1}{\sqrt{2\pi}}$$

b) Eigenstates of \hat{L}_z :

$$\begin{cases} \frac{1}{\sqrt{2\pi}}e^{ik\phi} \\ \frac{1}{\sqrt{2\pi}}e^{-ik\phi} \end{cases}$$

c) Other choice, for example :

$$\begin{cases} \frac{1}{\sqrt{\pi}}\sin(k\phi + \alpha) \\ \frac{1}{\sqrt{\pi}}\cos(k\phi + \alpha) \end{cases}$$

α for arbitrary.

More details about Particle on a Ring, see Link: [Particle on a Ring](#).

4.4.2 Consequences of Symmetry: Multiplet

Consider a multiplet of eigenstates of Hamiltonian, $|\phi_k\rangle$, all with same energy, E . The number of orthonormal states is well defined as degeneracy. States themselves are called freedom. The space it spans is always the same.

$$\sum_{k \in E} |\phi_k\rangle\langle\phi_k| = \hat{P}_E \quad (66)$$

NOTE:

\hat{P}_E is a projector on this space.

Then for any symmetry operator \hat{u}^a :

$$\hat{H}(\hat{u}^a|\phi_n\rangle) = E_n(\hat{u}^a|\phi_n\rangle) \quad (67)$$

Hence, \hat{u}^a is a linear combination of states in the multiplet.

$$\begin{aligned} \hat{u}^a|\phi_l\rangle &= \sum_{l \in P_E} |\phi_l\rangle\langle\phi_l|\hat{u}^a|\phi_k\rangle \\ &= \sum_{l \in P_E} |\phi_l\rangle\hat{u}_{lm}^a \end{aligned} \quad (68)$$

Likewise:

$$\hat{u}^b |\phi_l\rangle = \sum_{l \in P_E} |\phi_m\rangle \hat{u}_{ml}^b \quad (69)$$

The important point is that $\hat{u} |\phi_k\rangle$ can always be expressed in terms of the states in the multiplet.
 → Stay in the subspace.

$$\hat{u}^b \hat{u}^a |\phi_l\rangle = \sum_{m, l \in P_E} |\phi_m\rangle \langle \phi_m | \hat{u}^b |\phi_l\rangle \langle \phi_l | \hat{u}^a |\phi_k\rangle \quad (70)$$

$$= \sum_{m, l \in P_E} |\phi_m\rangle \hat{u}_{ml}^b \hat{u}_{lk}^a \quad (71)$$

$$\equiv |\phi_m\rangle \hat{u}_{mk}^{ba} \quad (72)$$

It follows that the matrix-elements of the symmetry operator, follow the same multiplication law as the group.

$$\hat{u}^{ba} = \hat{u}^b \hat{u}^a \quad \forall a, b \quad (73)$$

⇒ Group multiplication \iff Matrix multiplication

The dimension of the matrices is the same as degeneracy of Hamiltonian.

4.4.3 Consequences of Symmetry: Irreducible Representations

Group theory: The matrices \hat{u}^a form a representation of a group.

■ Example:

H-atom : 1s (non-degenerate)

Rotations: 1-dimensional matrices (just numbers)

p-orbitals (p_x, p_y, p_z) : 3-dimensional matrices (3-dimensional representation).

d-orbitals ($d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$) : 5-dimensional matrices (5-dimensional representation).

⇒ We get the representations of groups.

⇒ Heart of group theory.

If one cannot reduce the set of functions further, i.e one cannot find a new basis in which all matrices \hat{u}^a have a block form. Then the representation is called irreducible.

Functions $|\phi_l\rangle$: transform according to irreducible representations.

The eigenstates of the Hamiltonian can always be chosen to transform as irreducible representations of the symmetry group of \hat{H} .

$$\phi_n |n, \Gamma, i\rangle \quad (74)$$

NOTE:

Γ : irreducible representation.

i : column of irrep.

n : labels different multiplets, different energy E_n .

$$y_l^m(\theta, \psi) \quad \text{Spherical Harmonics} \quad (75)$$

NOTE:

l : label of irrep.

m : different columns of irrep.

For many electron atoms, we use the same angular momentum label S, P, D, F and can label functions as (L, M) .

\Rightarrow irreducible representations (same as orbitals)

For molecules: Orbitals and many-electron wave functions transform as irreducible representations: A_1, B_1, B_2, A_2 for water, C_{2v} etc.

The irreducible representations are determined by the symmetry group. Independent of Hamiltonian. One can show:

$$\langle \phi_k, \Gamma_1, i_1 | \hat{H} | \phi_l, \Gamma_2, i_2 \rangle = 0 \quad (76)$$

NOTE:

unless $\Gamma_1 = \Gamma_2$ same irrep.

unless $\Gamma_1 = \Gamma_2$ same column.

k labels different functions all transforming as Γ_1, i

Only functions that 'interact' have the same symmetry. Interaction means make matrix-elements of Hamiltonian.

\Rightarrow The Hamiltonian is block diagonal in a symmetry-adapted basis.

Example (water, C_{2v}):

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	+1	+1	-1	-1	R_z	xy	xyz
B_1	+1	-1	+1	-1	x, R_y	xz	xz^2, x^3, xy^2
B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

Figure 3 Character table for point group C_{2v} .

Only need to diagonalize blocks: cost of diagonalizations $\sim n^3$

h blocks: h diagonalizations of $\sim n/h$ blocks. cost, $h(n/h)^3 = \frac{1}{h^2}n^3$.

Symmetry:

a) Symmetry can be very important to use to make calculation more efficient.

- b) States can be labelled according to symmetry \Rightarrow qualitative understanding, degeneracy pattern.

The use of irreducible representations is the most elaborate use of symmetry in Quantum chemistry.

\Rightarrow It is all 'just' group theory (math). Any correct results in math will never change.

More details about Irreducible Representations:

See Link: [Wikipedia Website Link on Irreducible Representations](#)

4.5 Complete Set of Commuting Operators

Alternate way to think of symmetry: complete set of commuting operators.

Let \hat{A}, \hat{B} be Hermitian operators that commute with \hat{H} , and also with each other. (unitary operators are usually not Hermitian)

$$[\hat{H}, \hat{A}] = [\hat{H}, \hat{B}] = [\hat{A}, \hat{B}] = 0 \quad (77)$$

Example: $\hat{H}, \hat{L}^2, \hat{L}_z$

Hermitian operator: $\hat{O}|O_i\rangle = O_i|O_i\rangle$ Get eigenvalues and eigenvectors.

Then, we can define a complete set of common eigenstates $|E_n, a_i, b_j\rangle$.

$$\hat{H}|E_n, a_i, b_j\rangle = E_n|E_n, a_i, b_j\rangle \quad (78)$$

$$\hat{A}|E_n, a_i, b_j\rangle = a_i|E_n, a_i, b_j\rangle \quad (79)$$

$$\hat{B}|E_n, a_i, b_j\rangle = b_j|E_n, a_i, b_j\rangle \quad (80)$$

Simultaneous, eigenstates of $\hat{H}, \hat{A}, \hat{B}$.

If \hat{A}, \hat{B} have complete set of common eigenstates then $[\hat{A}, \hat{B}] = 0$

$$[\hat{A}, \hat{B}] = 0 \xLeftrightarrow[(1),(2)] \text{ complete set of common eigenstates}$$

Proof (1):

Complete basis: $|\psi\rangle = \sum_{i,j} |a_i, b_j\rangle c_{ij}$

Any ψ can be expanded in $|a_i, b_j\rangle$

$$\begin{aligned} \hat{A}\hat{B}|a_i, b_j\rangle &= \hat{A}(b_j|a_i, b_j\rangle) \\ &= a_i b_j |a_i, b_j\rangle \end{aligned} \quad (81)$$

$$\begin{aligned} \hat{B}\hat{A}|a_i, b_j\rangle &= \hat{B}(a_i|a_i, b_j\rangle) \\ &= b_j a_i |a_i, b_j\rangle \end{aligned} \quad (82)$$

$$\begin{aligned} (\hat{A}\hat{B} - \hat{B}\hat{A})|\psi\rangle &= (\hat{A}\hat{B} - \hat{B}\hat{A}) \sum_{i,j} |a_i, b_j\rangle c_{ij} \\ &= \sum_{i,j} (a_i b_j - b_j a_i) c_{ij} = 0 \quad \forall \psi \end{aligned} \quad (83)$$

Reverse the order of the eigenvalues, and eigenvalues are numbers.

Proof (2):

The converse part: if $[\hat{A}, \hat{B}] = 0$, they have a complete set of common eigenstates is most involved, but instructive:

First, diagonalize the operator \hat{B} : $\hat{B}|b_j\rangle = b_j|b_j\rangle$.

Reverse order: $(\hat{B}^\dagger|b_i\rangle)^\dagger = \langle b_i|\hat{B}$.

Hermitian operator: $\hat{B}^\dagger = \hat{B}$.

Eigenvalues of Hermitian operator are real: $\hat{B}^\dagger = \langle b_i|b_i\rangle^\dagger = \langle b_i|b_i^* = \langle b_i|b_i$

Acting with \hat{B} on bra directly.

Analogue: right and left eigenvectors for matrices.

For Hermitian/Symmetric matrices eigenvectors are same (or hermitian conjugate).

Eigenvalues are the same.

$$\langle b_i|[\hat{A}, \hat{B}]|b_j\rangle = 0 \quad (84)$$

$$\langle b_i|\hat{A}\hat{B} - \hat{B}\hat{A}|b_j\rangle = 0 \quad (85)$$

$$(b_i - b_j)\langle b_i|\hat{A}|b_j\rangle = 0 \quad (86)$$

\Rightarrow If $b_i \neq b_j$, then:

$$\langle b_i|\hat{A}|b_j\rangle = 0 \quad (87)$$

$\Rightarrow \hat{A}$ is block diagonal in \hat{B} basis.

Second, diagonalize the \hat{A} :

\hat{A}	b_1	b_2	b_3
b_1	x	0	0
b_2	0	x	0
b_3	0	0	x

\hat{A} is block-diagonal.

I can diagonalize each block by itself. This does not change eigenvalue of \hat{B} .

All states in a b_i block have same eigenvalues.

$$\hat{A}|a_i, b_j\rangle = a_i|a_i, b_j\rangle \quad (88)$$

$$\hat{B}|a_i, b_j\rangle = b_j|a_i, b_j\rangle \quad (89)$$

This procedure can be repeated including additional commuting operators.

$$\begin{aligned} \hat{B} \sum_k |b_j, k\rangle c_k &= \sum_k b_j |b_j, k\rangle c_k \\ &= b_j \left(\sum_k |b_j, k\rangle c_k \right) \end{aligned} \quad (90)$$

Linear combination of states with same eigenvalue b_j is eigenstate of \hat{B} with eigenvalue b_j .

If three operators are commuting $[\hat{A}, \hat{B}] = [\hat{A}, \hat{C}] = [\hat{B}, \hat{C}] = 0$, the complete set of eigenstates is $|a_i, b_j, c_k\rangle$.

⇒ These all present good quantum numbers.

⇒ Labels for the states.

e.g. $\hat{H}, \hat{L}^2, \hat{L}_z \longrightarrow |E_n, l, m\rangle$

e.g. $\hat{S}_1^2, \hat{S}_z \longrightarrow |E_n, L, M, S, M_s\rangle$

In a time-dependent formulation $\langle \hat{A} \rangle$ and $\langle \hat{B} \rangle$ would not depend on time.

$$\begin{aligned}\langle \psi(t) | \hat{A} | \psi(t) \rangle &= \langle \psi(t=0) | e^{i\hat{H}t} \hat{A} e^{-i\hat{H}t} | \psi(t=0) \rangle \\ &= \langle \psi(t=0) | \hat{A} | \psi(t=0) \rangle\end{aligned}\quad (91)$$

\hat{H} is independent of time.

$$[\hat{H}, \hat{A}] = 0 \quad (92)$$

$$\frac{d\langle \hat{A} \rangle}{dt} = 0 \quad (93)$$

$$[\hat{H}, f(\hat{A})] = 0 \quad f(\hat{A}): \text{Taylor series expansion} \quad (94)$$

$$[\hat{H}^n, \hat{A}] = 0 \quad (95)$$

Such operators represent conserved quantities.

Any Hermitian operator that has $[\hat{H}, \hat{A}] = 0$ is a conserved quantity.

$$\hat{A}^\dagger = \hat{A} \quad (96)$$

$$(e^{i\hat{A}})^\dagger = e^{(i\hat{A})^\dagger} = e^{-i\hat{A}^\dagger} = e^{-i\hat{A}} \quad (97)$$

$$e^{i\hat{A}}(e^{i\hat{A}})^\dagger = e^{i\hat{A}}e^{-i\hat{A}} = 1 \quad (98)$$

NOTE:

\hat{A} : hermitian operator.

$e^{i\hat{A}}$ is a symmetry operator, or even $e^{i\hat{A}\alpha}$ is symmetry operator with real parameter α .

This is a way to make the connection between symmetries and conserved quantities.

Example(1):

$\hat{L}_x, \hat{L}_y, \hat{L}_z$ are hermitian, commute with \hat{H} .

$$\hat{L}_\pm = \hat{L}_x \pm i\hat{L}_y \quad (99)$$

$$\hat{L}_+ |l, m\rangle \longrightarrow c_+ |l, m+1\rangle \quad \hat{L}_- |l, m\rangle \longrightarrow c_- |l, m-1\rangle$$

$$[\hat{H}, \hat{L}_\pm] = 0 \quad (100)$$

$$[\hat{H}, \hat{L}_\pm] = 0 \quad (101)$$

\hat{L}_+, \hat{L}_- create new eigenstates with same eigenvalue.

$e^{\alpha\hat{L}_x+\beta\hat{L}_y+\gamma\hat{L}_z}$ is an operator that defines wave functions in a rotated frame.

These symmetries are continuous symmetries group described by linear algebras.

Example(2):

\hat{p}_x commutes with free-particle motion $\hat{h} = -\frac{1}{2}\frac{d^2}{dx^2}$, which means $[\hat{p}_x, \hat{h}] = 0$.

$e^{ia\hat{p}_x}|\psi(x)\rangle$ creates translated function.

$$e^{ia\hat{p}_x} = e^{ia(-i\hbar\frac{\partial}{\partial x})} = e^{a\hbar\frac{\partial}{\partial x}} \longrightarrow e^{b\frac{\partial}{\partial x}} \quad \text{with } b = a\hbar \quad (102)$$

$$\begin{aligned} e^{b\frac{\partial}{\partial x}}f(x) &= f(x) + b\frac{\partial f}{\partial x} + \frac{1}{2}b^2\frac{\partial^2 f}{\partial x^2} + \cdots + \frac{1}{n!}b^n\frac{\partial^n f}{\partial x^n} \\ &= f(x+b) \end{aligned} \quad (103)$$

NOTE: Taylor series expansion.

There are many aspects to symmetry. We often perceive symmetry as beautiful. The theory of symmetries is also very beautiful (group theory). For we personally, the study of group theory (independent reading class) was the first made me want to be a ‘theoretical chemist’.