Operators & Commutators

Quantum Operators: Physical observables are represented by linear, Hermitian operators acting on the wavefunction.

- *Linear operator:* $\hat{A}$ is linear if $\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1\hat{A}\psi_1 + c_2\hat{A}\psi_2$.
- *Hermitian (self-adjoint):* $\hat{A}$ satisfies $\langle\phi|\hat{A}|\psi\rangle = \langle\psi|\hat{A}|\phi\rangle^*$, which guarantees real eigenvalues and orthogonal eigenfunctions.
- *Eigenvalue equation:* $\hat{A}\phi_n = a_n\phi_n$. Measurement of observable A yields eigenvalue a_n with eigenstate ϕ_n.
- *Commutator:* $[\hat{A},\hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$. If $[\hat{A},\hat{B}] = 0$, then $\hat{A}$ and $\hat{B}$ share a common set of eigenstates (they are *simultaneously measurable*).

Important Operators: Identity $\hat{1}$ (unity, $\hat{1}\psi = \psi$); momentum $\hat{p} = -i\hbar\nabla$; position $\hat{x}$ (multiplication by x); Hamiltonian $\hat{H}$ (total energy operator).

Angular Momentum: Components $\hat{J}_x, \hat{J}_y, \hat{J}_z$ obey $[\hat{J}_x, \hat{J}_y] = i\hbar\,\hat{J}_z$ (and cyclic permutations). In general $[J_i, J_j] = i\hbar\epsilon_{ijk}J_k$. Raising/lowering operators $J_\pm = J_x \pm iJ_y$ satisfy $J_+|j,m\rangle \propto |j,m+1\rangle$.

Uncertainty Principle: For two Hermitian operators $\hat{A}$ and $\hat{B}$:

$$\boxed{\Delta A\,\Delta B \geq \frac{1}{2}\left|\langle[\hat{A},\hat{B}]\rangle\right|},$$

where $(\Delta A)^2 = \langle A^2\rangle - \langle A\rangle^2$ is the variance. In particular, $[\hat{x},\hat{p}] = i\hbar$ implies $\Delta x\,\Delta p \geq \hbar/2$.

Constants of Motion: If an operator commutes with the Hamiltonian ($[\hat{H},\hat{A}] = 0$), then A is conserved (constant in time). For a time-independent Hamiltonian, $\frac{d}{dt}\langle\hat{A}\rangle = \frac{i}{\hbar}\langle[\hat{H},\hat{A}]\rangle$. Thus, observables that commute with $\hat{H}$ correspond to conserved quantities.

Group Theory

Molecular Symmetry: The set of all symmetry operations (rotations, reflections, inversions, etc.) that leave a molecule unchanged forms a *point group*. Each symmetry operation corresponds to a group element. A group must satisfy:

- *Closure:* Combining any two group elements yields another element of the group.
- *Associativity:* $(AB)C = A(BC)$ for any elements A, B, C.
- *Identity:* There is an identity E such that $AE = EA = A$ for all A.
- *Inverse:* For each A, there is an inverse A^{-1} with $AA^{-1} = A^{-1}A = E$.

Representations: A representation maps each group element to a matrix (or linear operator) such that group multiplication corresponds to matrix multiplication. *Irreducible representations (irreps)* are representations that cannot be reduced (no smaller invariant subspace). The *character* $\chi(R)$ of a representation for operation R is the trace of its matrix. Characters for all irreps are summarized in a **character table**. For example:

Character Table of C_{2v}

Irrep	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Each row is an irrep (A_1, A_2, B_1, B_2 for C_{2v}); each column is a symmetry operation class. Characters indicate how a basis function transforms under each operation.

Orthogonality Theorems: Characters of irreps are orthonormal (Great Orthogonality Theorem leads to character orthonormality). For group order h:

$$\boxed{\text{LOT: } \frac{1}{h}\sum_R \chi^{(\alpha)}(R)\,\chi^{(\beta)}(R)^* = \delta_{\alpha\beta}},$$

$$\boxed{\text{BOT: } \frac{1}{h}\sum_\alpha \chi^{(\alpha)}(R)\,\chi^{(\alpha)}(R')^* = \delta_{RR'}},$$

where LOT (Little Orthogonality Theorem) shows different irreps $\alpha \neq \beta$ have orthogonal character rows, and BOT (Big Orthogonality Theorem) shows orthogonality of columns (classes). These imply the number of irreps equals the number of classes.

Reducibility: Any representation can be expressed as a direct sum of irreps. The characters of a reducible representation Γ can be decomposed using $\langle\Gamma,\alpha\rangle = \frac{1}{h}\sum_R \chi^\Gamma(R)\chi^{(\alpha)}(R)^*$ to find how many times irrep α appears.

Selection Rules: Symmetry dictates allowed transitions and interactions. An integral (e.g. transition dipole $\langle\psi_i|\mu|\psi_f\rangle$) is nonzero only if the overall symmetry of the integrand contains the totally symmetric representation. In other words, the product of irreps for initial state, operator, and final state must include A_1 (for C_{2v}). Symmetry thus predicts spectral lines and degeneracies.

Time Dependence & Perturbation

Schrödinger Equation: Quantum dynamics are governed by the time-dependent Schrödinger equation

$$\boxed{i\hbar\frac{\partial}{\partial t}\Psi(r,t) = \hat{H}\,\Psi(r,t)},$$

which for a time-independent Hamiltonian yields solutions $\Psi_n(r,t) = \psi_n(r)e^{-iE_nt/\hbar}$. The spatial part $\psi_n(r)$ satisfies the time-independent Schrödinger equation (TISE):

$$\boxed{\hat{H}\,\psi_n(r) = E_n\,\psi_n(r)},$$

an eigenvalue problem defining stationary states and quantized energies E_n.

Time Evolution Operator: For time-independent $\hat{H}$, $\hat{U}(t) = e^{-i\hat{H}t/\hbar}$ evolves states: $|\Psi(t)\rangle = \hat{U}(t)|\Psi(0)\rangle$. If $[\hat{H},\hat{A}] = 0$, then $\hat{A}$ is constant in time (Heisenberg picture: operators evolve as $\hat{A}(t) = e^{iHt/\hbar}\hat{A}(0)e^{-iHt/\hbar}$).

Time-Independent Perturbation: Suppose $\hat{H} = \hat{H}^{(0)} + \lambda\hat{V}$, with λ small. For non-degenerate case, zeroth-order solutions are $\hat{H}^{(0)}|n^0\rangle = E_n^0|n^0\rangle$. The corrections are found as power series in λ: $E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2E_n^{(2)} + \cdots$, and $|n\rangle = |n^0\rangle + \lambda|n^{(1)}\rangle + \cdots$. The first-order and second-order energy corrections are:

$$\boxed{E_n^{(1)} = \langle n^0|\hat{V}|n^0\rangle}, \qquad \boxed{E_n^{(2)} = \sum_{m\neq n}\frac{|\langle m^0|\hat{V}|n^0\rangle|^2}{E_n^0 - E_m^0}}.$$

The first-order correction shifts E_n by the diagonal matrix element of $\hat{V}$. The second-order term accounts for virtual transitions to other states $m \neq n$. The perturbed eigenstate to first order is

$$|n^{(1)}\rangle = \sum_{m\neq n}\frac{\langle m^0|\hat{V}|n^0\rangle}{E_n^0 - E_m^0}\,|m^0\rangle,$$

showing that $\hat{V}$ mixes in a small component of other eigenstates.

Time-Dependent Perturbation: If a perturbation $\hat{V}(t)$ is applied (e.g. an oscillating electromagnetic field), transitions between states can occur. For a perturbation turned on at $t = 0$, time-dependent perturbation theory gives transition amplitudes via time integrals. In the case of a constant perturbation (or monochromatic perturbation at resonance), *Fermi's Golden Rule* provides the transition rate from initial state i to final state f:

$$\boxed{W_{i\to f} \;=\; \frac{2\pi}{\hbar}\,|\langle f|\hat{V}|i\rangle|^2\,\rho(E_f)},$$

where $\rho(E_f)$ is the density of final states at energy E_f. This rule (derived as a first-order perturbative result for long times) says the transition probability per unit time is proportional to the square of the matrix element of the perturbation between $|i\rangle$ and $|f\rangle$, and to the number of final states available at that energy.

Selection Rules (TD): The time-dependent perturbation (often an oscillating field) usually has specific symmetry (e.g. an electric dipole interaction is odd under inversion). Thus, transitions occur only between states of appropriate symmetry. For example, electric dipole transitions require $\langle f|\hat{\mu}|i\rangle \neq 0$, which typically means the parity (or overall symmetry) of $|f\rangle$ and $|i\rangle$ differ. Group theory can predict these rules (e.g. in a character table, x, y, z coordinates often belong to certain irreps, indicating allowed dipole transition directions).

Electronic Structure Theory

Born-Oppenheimer (BO) Approximation: Simplifies the molecular Schrödinger equation by decoupling nuclear and electronic motions. Because nuclei are much heavier and move slower, one assumes nuclei are nearly fixed while solving for electronic wavefunctions. The total wavefunction is written as $\Psi(r,R) \approx \psi_{\text{el}}(r;R)\,\chi_{\text{nuc}}(R)$, where r denotes electronic coordinates and R nuclear coordinates. $\psi_{\text{el}}(r;R)$ solves the electronic Schrödinger equation for fixed R:

$$\hat{H}_{\text{el}}(r;R)\,\psi_{\text{el}}(r;R) = E_{\text{el}}(R)\,\psi_{\text{el}}(r;R),$$

yielding an electronic energy $E_{\text{el}}(R)$ (the potential energy surface for nuclear motion). $\chi_{\text{nuc}}(R)$ then solves the nuclear equation with $E_{\text{el}}(R)$ as part of its potential. The BO approximation thus breaks the full problem into an electronic part and a nuclear part, greatly reducing complexity.

Antisymmetry and Spin: Electrons are fermions, so the N-electron wavefunction must be antisymmetric under exchange of any two electrons (Pauli exclusion principle). One convenient way to ensure this is using a *Slater determinant.* For example, with two electrons:

$$\Psi(1,2) = \frac{1}{\sqrt{2!}}(\phi_a(1)\,\phi_b(2) - \phi_a(2)\,\phi_b(1)),$$

which is antisymmetric under exchange of electrons 1 and 2. Here ϕ_a, ϕ_b are single-electron spin-orbitals (each a spatial orbital times a spin state). In general, a Slater determinant for N electrons is the $N \times N$ determinant of N spin-orbitals, normalized by $1/\sqrt{N!}$.

Hartree–Fock (HF) Method: Approximates the multi-electron wavefunction by a single Slater determinant (a single configuration). It yields the *Hartree–Fock equations* for the orbitals:

$$\boxed{\hat{F}\,\phi_i = \epsilon_i\,\phi_i},$$

where $\hat{F}$ is the Fock operator (an effective one-electron Hamiltonian). $\hat{F}$ includes the kinetic energy and nuclear attraction (the one-electron part $\hat{h}$), plus electron-electron repulsion in an averaged way:

$$\hat{F} = \hat{h} + \sum_{j\,\mathrm{occ}} \big(\hat{J}_j - \hat{K}_j\big).$$

Here $\hat{J}_j$ is the Coulomb operator (it computes the electrostatic repulsion due to an electron in orbital j) and $\hat{K}_j$ is the exchange operator (arising from antisymmetry; it has no classical analog). Each orbital ϕ_i is solved in the field of the other electrons; the solutions are obtained self-consistently (the HF procedure: guess orbitals, construct $\hat{F}$, solve for new orbitals, and repeat until convergence). The resulting orbital energies ϵ_i and orbitals ϕ_i approximate the true multi-electron solution. The total HF energy is

$$E_{\mathrm{HF}} = \sum_{i}^{\mathrm{occ}} \langle\phi_i|\hat{h}|\phi_i\rangle + \frac{1}{2}\sum_{i,j}^{\mathrm{occ}} \Big(\langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|\frac{1}{r_{12}}|\phi_j\phi_i\rangle \Big),$$

where the two terms in the double sum are the Coulomb (J_{ij}) and exchange (K_{ij}) integrals. (The 1/2 avoids double-counting pair interactions.)

Electron Correlation: HF is a mean-field theory and neglects electron correlation (the instantaneous interactions between electrons beyond the average field). The difference $E_{\mathrm{exact}} - E_{\mathrm{HF}}$ is the *correlation energy.* To recover correlation and improve accuracy, *post-Hartree–Fock* methods are used:

- *Møller–Plesset perturbation theory (MP2, MP3, ...):* Treats the electron-electron interaction beyond HF as a perturbation. MP2 (second order) often gives a first estimate of correlation energy.
- *Configuration Interaction (CI):* Expands the wavefunction in a linear combination of Slater determinants (configurations). For example, CI singles and doubles (CISD) includes one- and two-electron excitations out of the HF determinant. Full CI (all excitations in a given basis) is exact within that basis but grows combinatorially with system size.
- *Coupled Cluster (CC):* Uses an exponential ansatz $|\Psi\rangle = e^{\hat{T}}|\Phi_{\mathrm{HF}}\rangle$, where $\hat{T}$ is a cluster operator (e.g. T_1 and T_2 for single and double excitations). CCSD(T), which includes singles, doubles, and perturbative triples, is often considered the "gold standard" for quantum chemistry due to its high accuracy.
- *Multi-Configurational SCF (MCSCF):* Allows multiple Slater determinants and optimizes both orbitals and expansion coefficients self-consistently. For example, CASSCF (Complete Active Space SCF) is used for situations with strong static correlation (when one determinant is insufficient, such as bond breaking).

Density Functional Theory (DFT): An alternative approach using the electron density $\rho(\mathbf{r})$ as the primary variable instead of the wavefunction. The Hohenberg–Kohn theorems (1964) state that the ground-state energy is a unique functional of ρ, and the true ρ minimizes this energy functional. Kohn–Sham DFT (1965) introduces a set of orbitals to represent ρ and divides the energy into kinetic, electron-nuclear, Coulomb (Hartree), and exchange-correlation $E_{xc}[\rho]$ terms. In practice, one solves Kohn–Sham equations, which resemble HF equations:

$$\Big(-\frac{\hbar^2}{2m}\nabla^2 + V_{\mathrm{ext}}(\mathbf{r}) + V_H[\rho](\mathbf{r}) + V_{xc}[\rho](\mathbf{r})\Big)\,\phi_i(\mathbf{r}) = \epsilon_i\,\phi_i(\mathbf{r}),$$

where V_H is the Hartree (Coulomb) potential from ρ and V_{xc} is the exchange-correlation potential derived from $E_{xc}[\rho]$. DFT includes electron correlation effects through approximate E_{xc} functionals (LDA, GGA, hybrid, etc.) at a lower computational cost than explicit multi-electron wavefunction methods. It is widely used for large systems, though its accuracy depends on the chosen functional.