# HERMITIAN OPERATORS

### 1. DIRAC NOTATION

We first introduce a notation that is due to Dirac. The idea is to reduce notational clutter and give more prominence to the labels identifying the wavefunctions.

In this notation, a **ket**  $|n\rangle$  is used for the wavefunction  $\psi_n$ . A **bra**  $\langle n|$  is used to denote the complex conjugate of the wavefunction,  $\psi_n^*$ . A complete *bra-ket* notation, such as  $\langle n|n\rangle$  or  $\langle n|\hat{Q}|n\rangle$ , implies integration over all space. For example, we have

$$\langle n|n 
angle = \int \psi_n^* \psi_n d au$$
  
 $\langle n|\hat{Q}|n 
angle = \int \psi_n^* \hat{Q} \psi_n d au$ 

## 2. Hermiticity

Every operator  $\hat{Q}$  has a *Hermitian conjugate*, conventionally denoted  $\hat{Q}^{\dagger}$ , which has the following property for any two wavefunctions  $\psi_m$  and  $\psi_n$  satisfying the boundary conditions for the system:

$$\int \psi_m^* \hat{Q} \psi_n d\tau = \int (\hat{Q}^\dagger \psi_m)^* \psi_n d\tau \tag{1}$$

We can write the above using Dirac notation as

$$\langle m | \hat{Q} | n \rangle = \left\langle \hat{Q}^{\dagger} m | n \right\rangle.$$
 (2)

An operator is **Hermitian** if it is equal to its Hermitian conjugate, i.e.,  $\hat{Q} = \hat{Q}^{\dagger}$ , such that Eq. (1) becomes

$$\int \psi_m^* \hat{Q} \psi_n d\tau = \int (\hat{Q} \psi_m)^* \psi_n d\tau \tag{3}$$

We note the following useful properties. If the operator  $\hat{Q}$  is Hermitian, then

$$\langle m | \hat{Q} | n \rangle = \int \psi_m^* \hat{Q} \psi_n d\tau = \int (\hat{Q} \psi_m)^* \psi_n d\tau = \left( \int \psi_n^* \hat{Q} \psi_m d\tau \right)^* = \langle n | \hat{Q} | m \rangle^* \quad (4)$$

Similarly,

$$\langle m|n\rangle = \int \psi_m^* \psi_n d\tau = \left(\int_1 \psi_n^* \psi_m d\tau\right)^* = \langle n|m\rangle^* \tag{5}$$

#### 3. PROPERTIES OF HERMITIAN OPERATORS

Any Hermitian operator has the following properties:

- (1) their eigenvalues are always real.
- (2) eigenfunctions corresponding to different eigenvalues are orthogonal.

*Proof:* Suppose we have two eigenfunctions of a Hermitian operator  $\hat{Q}$  such that

$$\hat{Q}\left|m\right\rangle = q_m\left|m\right\rangle \tag{6}$$

$$\hat{Q}\left|n\right\rangle = q_{n}\left|n\right\rangle \tag{7}$$

We can pre-multipy Eq. (6) by  $\psi_n^*$  and Eq. (7) by  $\psi_m^*$ , and integrate over all space to obtain

$$\langle n | \hat{Q} | m \rangle = q_m \langle n | m \rangle \tag{8}$$

$$\langle m | \hat{Q} | n \rangle = q_n \langle m | n \rangle \tag{9}$$

Taking the complex conjugate of Eq. (8), we get

$$\langle n|\,\hat{Q}\,|m\rangle^* = q_m^*\,\langle n|m\rangle^* \tag{10}$$

Now, using the properties in Eqs. (4) and (5), the above becomes

$$\langle m | \hat{Q} | n \rangle = q_m^* \langle m | n \rangle \tag{11}$$

Subtracting the above from Eq. (9), we have

$$0 = (q_n - q_m^*) \langle m | n \rangle \tag{12}$$

We can now deduce the following:

- (1) If m = n, then  $\langle m | n \rangle = \langle n | n \rangle \neq 0$ , so that  $q_n = q_n^*$ , therefore,  $q_n$  is real.
- (2) If  $q_m \neq q_n$ , then since both are real, thus  $(q_n q_m^*) \neq 0$ , therefore,  $\langle m | n \rangle = 0$ , i.e., the wavefunctions  $\psi_m$  and  $\psi_n$ , corresponding to different eigenvalues, are orthogonal.

We can therefore note that in quantum mechanics, any physical property is represented by a Hermitian operator since the measurement of the corresponding physical property must be real. Conversely, if an operator is not Hermitian, it cannot correspond to any physical property as its eigenvalues are not guaranteed to be real.

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### 4. Completeness Relation

The completeness relation is a cornerstone of quantum mechanics and linear algebra. At its core, it's a statement about the ability of a set of vectors to fully describe a vector space. In a finite K-dimension, a "completeness relation" for a set of vectors  $|\psi_n\rangle$  refers to the following relation

$$\sum_{n=1}^{K} |\psi_n\rangle \langle\psi_n| = \hat{1}, \tag{13}$$

where the right hand side is the unit or identity operator. Each term  $|\psi_n\rangle \langle \psi_n|$ is a projection operator, which extracts the component of a vector along  $|\psi_n\rangle$ . Summing these projectors over all K basis vectors yields the identity operator, meaning that for any vector  $|\phi\rangle$  in the space:

$$|\phi\rangle = \sum_{n=1}^{K} |\psi_n\rangle \langle\psi_n|\phi\rangle.$$
(14)

This reconstruction works because the projections collectively account for every direction in the K-dimensional space, ensuring no part of the space is inaccessible. In other words, the completeness relation guarantees that the set  $\{|\psi_n\rangle\}$  includes enough and right vectors to span the entire space without omission, a property ensured by having exactly K orthonormal vectors in a K-dimensional space.

4.1. **Implications in Quantum Chemistry.** The completeness relation is fundamental in quantum mechanics:

- Resolution of Identity: It allows any wavefunction to be expanded in the basis, e.g.,  $|\Psi\rangle = \sum_n c_n |\psi_n\rangle$ , where  $c_n = \langle \psi_n | \Psi \rangle$ .
- Matrix Elements: For an operator  $\hat{A}$ , the matrix representation is  $A_{ij} = \langle \psi_i | \hat{A} | \psi_j \rangle$ , and completeness ensures all contributions are captured. Wave mechanics and matrix mechanics are equivalent.
- Degenerate Subspaces: Within an  $m_i$ -dimensional eigenspace, the  $m_i$  orthonormal vectors satisfy a local completeness relation, e.g.,  $\sum_{n=1}^{m_i} |\psi_n\rangle \langle \psi_n| = \hat{1}_{m_i}$ , the identity on that subspace.

In quantum chemistry, this underpins methods like spectral decomposition of the Hamiltonian or computing expectation values, ensuring the basis fully describes the system.

#### 5. Degenerate eigenvalues

When eigenvalues are degenerate, the eigenvectors associated with a single eigenvalue form an eigenspace of dimension equal to the multiplicity of that eigenvalue (number of times that the same eigenvalue repeats). Within this eigenspace, the ©Xinglong Zhang 2017 3

eigenvectors are **not** naturally orthogonal—they are just linearly independent (and even then, only if chosen appropriately). For example, if an eigenvalue  $\lambda$  has a multiplicity 3, its eigenspace is 3-dimensional, and we can pick *any* basis of 3 *linearly independent* vectors for it.

Now, consider a K-dimensional vector space and a matrix  $\mathbf{A}$  (e.g., a Hamiltonian operator) with A eigenvectors consisting of the following:

- *M* eigenvectors, corresponding to degenerate eigenvalues.
- K M eigenvectors, each with a unique eigenvalue (multiplicity 1).

We can create an orthonormal basis spanning the full space, i.e., to satisfy the completeness relation. For the Hermitian matrix  $\mathbf{A}$ , the eigenvectors corresponding to distinct eigenvalues are automatically orthogonal. So, these K - M vectors are orthogonal to each other. However, they are not necessarily orthogonal to the M vectors with degenerate eigenvalues, and none of them are guaranteed to be normalized.

5.1. **Gram-Schmidt process.** The Gram-Schmidt process transforms a set of linearly independent vectors  $\{v_1, v_2, \ldots, v_n\}$  into an orthonormal set  $\{u_1, u_2, \ldots, u_n\}$ , where:

$$u_{1} = \frac{v_{1}}{\|v_{1}\|}, \quad u_{k} = \frac{v_{k} - \sum_{j=1}^{k-1} \langle u_{j}, v_{k} \rangle u_{j}}{\|v_{k} - \sum_{j=1}^{k-1} \langle u_{j}, v_{k} \rangle u_{j}\|}, \quad k = 2, \dots, n$$

Thus, to form an orthonormal basis for the entire K-dimensional vector space, we need to

- (1) Orthogonalize within degenerate eigenspaces: Apply Gram-Schmidt to the M eigenvectors, grouped by their eigenvalues. If all M vectors correspond to one degenerate eigenvalue of multiplicity m, you orthogonalize all M vectors together. If they split across multiple eigenvalues, do it separately for each eigenspace.
- (2) Combine with the K M vectors: Take the resulting M orthonormal vectors and the K M vectors as a set of K vectors.
- (3) Full Gram-Schmidt: Since the K M vectors (with unique eigenvalues) may not be orthogonal to the M vectors, apply Gram-Schmidt to the entire set of K vectors, ensuring the process respects the eigenspaces:
  - Start with the M orthonormal vectors from step 1.
  - For each of the K M vectors, subtract their projections onto all previous vectors (including the M ones) and normalize.

5.2. Assumptions. This process assumes: ©Xinglong Zhang 2017

- A is diagonalizable with K linearly independent eigenvectors (true for Hermitian matrices). If A is not diagonalizable, we might not have enough eigenvectors.
- For degenerate eigenvalues, Gram-Schmidt handles degeneracy within eigenspaces, but the K M vectors must have distinct eigenvalues.
- The initial M vectors span their eigenspaces properly, i.e., they are linearly independent.
- 6. Implications of Completeness Relations in Quantum Chemistry

6.1. Quantum Mechanical Context. In quantum chemistry, the Hamiltonian  $\hat{H}$  governs a molecular system, and its eigenfunctions (wavefunctions) correspond to energy states. These eigenfunctions may be:

- Molecular orbitals in Hartree-Fock or DFT.
- Multi-electron wavefunctions in configuration interaction (CI).

Degeneracies arise from molecular symmetry (e.g., *p*-orbitals in atoms or  $t_{2g}$  orbitals in octahedral complexes). An orthonormal basis is crucial for computation and physical interpretation.

# 6.2. Key Implications.

6.2.1. *Orthonormality in Calculations*. Orthonormal bases simplify quantum chemical computations:

- Overlap integrals become  $\langle \psi_i | \psi_j \rangle = \delta_{ij}$ .
- In a non-orthogonal basis, we solve  $\mathbf{Hc} = E\mathbf{Sc}$  (generalized eigenvalue problem). Orthogonalization yields  $\mathbf{H'c} = E\mathbf{c}$ , reducing complexity.

For degenerate states (e.g.,  $e_g$  orbitals in benzene), Gram-Schmidt ensures orthonormality within the subspace, aiding methods like CI or perturbation theory.

6.2.2. *Symmetry and Degeneracy.* Molecular symmetry leads to degenerate energy levels. For example:

- In *H*-atom,  $2p_x$ ,  $2p_y$ ,  $2p_z$  are degenerate; Gram-Schmidt orthogonalizes them.
- In methane  $(T_d)$ ,  $t_2$  orbitals are triply degenerate.

Orthogonalizing within these subspaces respects symmetry and prepares the basis for perturbations (e.g., Jahn-Teller effects). ©Xinglong Zhang 2017 5 Hermitian Operators

6.2.3. *Physical Interpretability*. Orthonormality aligns with quantum mechanics' probabilistic nature:

$$|\langle \psi_i | \psi_j \rangle|^2 = \delta_{ij},$$

ensuring distinct states are separable. This clarity is vital for electron density or spectroscopic predictions.

6.2.4. *Perturbation Theory.* In degenerate perturbation theory, an orthonormal zeroth-order basis is required to compute corrections when degeneracy is lifted (e.g., by an external field). The M degenerate vectors, once orthonomalized, provide this foundation.

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