

Hermitian Operators and their Applications

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This paper presents an overview of Hermitian operators. The paper introduces the mathematical definition and properties of Hermitian operators, and then discusses their relevance in quantum mechanics. The one-dimensional particle in a box (PB) system is then discussed and its key principles derived in order to illustrate the use of Hermitian operators in solving quantum mechanical problems. A more complicated 3D PB model of excitons in conjugated polymers (polymers containing alternating single and double carbon-carbon bonds) is then described, portraying the utility of the model to actual physical systems.

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I. INTRODUCTION

An operator is a rule that transforms a given function into another function¹. For example, \hat{x} could be an operator that multiplies a given function $f(x)$ by x . If we let $f(x) = 2x + 3$, then $\hat{x}f(x) = 2x^2 + 3x$.

Moreover, let \hat{A} be an operator and $f(x)$ be a function on which \hat{A} can act. If \hat{A} operating on $f(x)$ returns the same function $f(x)$ multiplied by a constant k , that is:

$$\hat{A}f(x) = kf(x), \quad (1)$$

then $f(x)$ is an eigenfunction of \hat{A} with eigenvalue k ¹.

Next, let \hat{A} be an operator and let ϕ and ψ represent any two arbitrary, well behaved functions. If the relation

$$\int \phi(\hat{A}\psi)^* d\tau = \int \psi^*(\hat{A}\phi) d\tau \quad (2)$$

is satisfied, where $d\tau$ is over all space, then \hat{A} is a Hermitian operator². Hermitian operators have two properties that form the basis of quantum mechanics. First, the eigenvalues of a Hermitian operator are real (as opposed to imaginary or complex). Second, the eigenfunctions of Hermitian operators are orthogonal to each other or can be made orthogonal by taking linear combinations of them. The proofs for these properties are described elsewhere^{1,2}.

II. QUANTUM MECHANICAL THEORY

In quantum mechanics, all of the dynamical information of a system is contained within a mathematical entity called the wavefunction³, often denoted as ψ . This information can be extracted from the wavefunction through the use of operators. Each physical property, or observable, of interest has a corresponding operator which operates on the wavefunction. If the wavefunction is an eigenfunction of that particular operator, then its eigenvalue is the value of that observable³. A prime example of this is embodied in the Schrödinger equation:

$$\hat{H}\psi = E\psi \quad (3)$$

Here \hat{H} is the Hamiltonian operator $-\frac{\hbar^2}{2m}\nabla^2 + V$, of which ψ is an eigenfunction, and E is the eigenvalue of ψ and corresponds to the total energy of the system.

Since observables are measurable physical quantities, the eigenvalues from which they are obtained must be real. Furthermore, in order to guarantee that the eigenvalues are real, the operators corresponding to observables must be Hermitian.

If a wavefunction is not an eigenfunction of a Hermitian operator corresponding to an observable, the average (or expectation) value of that property can still be calculated. The expectation value of a property with operator \hat{A} can be denoted as $\langle A \rangle$ and is defined as:

$$\langle A \rangle = \int \psi^* \hat{A} \psi d\tau, \quad (4)$$

where ψ is the normalized wavefunction and $d\tau$ is over all space².

Applying the second afore-mentioned property of Hermitian operators, wavefunctions with different eigenvalues for a particular observable operator must be orthogonal.

III. APPLICATIONS

The study of the problem of a particle in a box (PB) provides an instructive view in the application of Hermitian operators in quantum mechanics. Within this model, a particle is assumed to be confined in a box of constant length. Inside this box, the potential V is taken to be zero, while outside the box, the potential is infinite². Although this model may appear crude at first glance, for reasons to be explained shortly, it works surprisingly well in calculating the electronic excitations of cyanine dyes, with results typically within a few percent of experimental values⁴. In this model, the excited electron is confined to a box with length equal to that of the chain length of the molecule. The length of the chain is given by

$L = a(k+1) + b$, where a is the length of each $-\text{CH}=\text{CH}-$ unit ($\approx 249 \text{ pm}^4$), k is the number of such units in the chain, and b is the length of the terminating functional groups. Within this length, the electron is allowed to move more freely. The success of this model lies in the strong delocalization of the π -bond system of cyanines, resulting in little variation in bond length and potential along the chain⁴. Moreover, when this periodic variation in bond length and potential is accounted for via perturbation theory, the first-order corrections to the energy levels are zero, confirming the validity of the unperturbed model⁴.

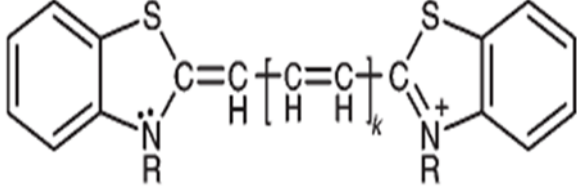


FIG. 1: Example Structure of a Cyanine Dye.⁴

Here a brief derivation of the one dimensional particle in a box model is given to illustrate the use of Hermitian operators¹⁻³. The particle is confined to a box from $0 < x < L$, where L is the length of the box, thus the wavefunction ψ outside the box equals zero. Inside the box, the potential $V(x)$ is zero, so the Schrödinger equation reduces to:

$$-\frac{\hbar^2}{2m}\nabla^2\psi = E\psi. \quad (5)$$

The solutions of this differential equation are of the form:

$$\psi = A \sin(\alpha x) + B \cos(\alpha x). \quad (6)$$

Due to the boundary condition that $\psi = 0$ at $x = 0$, B must equal zero. Additionally, due to the boundary condition that $\psi = 0$ at $x = L$, $\alpha = \frac{n\pi}{L}$, where n is a positive integer. The constant A is determined to be $\sqrt{\frac{2}{L}}$ by normalizing the wavefunction. To find the energy, the generic solution ψ is substituted back into the Schrödinger equation:

$$-\frac{\hbar^2}{2m}\nabla^2(A \sin(\frac{n\pi x}{L})) = E(A \sin(\frac{n\pi x}{L})). \quad (7)$$

From Equation (7) it can be shown that $E = \frac{n^2\hbar^2}{8mL^2}$. Since n is only to take allowed integer values, this shows that the energy levels of the system are quantized.

In order to further illustrate the use of Hermitian operators, the expectation value and uncertainty of the position for a PB particle are now calculated². The operator

corresponding to position is $\hat{x}\psi = x\psi$, so applying Equation 4:

$$\langle x \rangle = A^2 \int_0^L x \sin^2(\frac{n\pi x}{L}) dx \quad (8)$$

or $\langle x \rangle = \frac{L}{2}$, meaning that the average position of the particle is in the middle of the box. Using the same procedure, $\langle x^2 \rangle = \frac{L^2}{3}$. The uncertainty, or standard deviation, of the position of the particle can be calculated as follows²:

$$\Delta x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\frac{L^2}{12}} \quad (9)$$

The PB model for excitons in conjugated polymers (polymers containing alternating single and double carbon-carbon bonds) can be enhanced by expanding the box to three dimensions, accounting for both the electron and the electron hole, and deriving the Hamiltonian accordingly. The box is now of dimensions a , b and L in the respective x , y , and z directions, where the z axis is aligned with the chain of the molecule. The Hamiltonian is rewritten to take into account the kinetic energies of both the electron and the hole, the Coulombic attraction between the electron and the hole, and a static electric field of magnitude F along the chain (z) axis; meanwhile, the total energy is expressed in terms of the three-dimensional energy gap E_g^{3D} , which is the energy difference between the conduction band and valence band (see Figure (2)), and the exciton energy eigenvalue E_{eh} :



FIG. 2: Schematic showing bandgap, E_g^{3D} .⁸

$$\begin{aligned} & [-\frac{\hbar^2}{2m^*}(\nabla_e^2 + \nabla_h^2) + eFz_e - eFz_h - \\ & \frac{e^2}{4\pi\epsilon\epsilon_0|\vec{r}_e - \vec{r}_h|}] \Psi(\vec{r}_e, \vec{r}_h) = [E_{eh} - E_g^{3D}] \Psi(\vec{r}_e, \vec{r}_h) \end{aligned} \quad (10)$$

where the subscripts e and h denote quantities relating to the electron and the hole, respectively⁵ and m^* denotes the effective mass of the electron-hole pair⁶. The wavefunction can then be approximated as the following product:

$$\Psi(\vec{r}_e, \vec{r}_h) \approx \phi_a(x_e)\phi_a(x_h)\phi_b(y_e)\phi_b(y_h)\psi(z_e, z_h), \quad (10)$$

where ϕ_a and ϕ_b are the 1D PB wavefunctions⁵ derived earlier. These terms can then be integrated out⁷, leaving only the longitudinal wavefunction $\psi(z_e, z_h)$ in the z direction. The potential in the z direction can then be approximated as⁵:

$$V(z_e, z_h) = \frac{e^2}{4\pi\epsilon\epsilon_0} C(z) \quad (11)$$

Where $C(z) = C(z_e - z_h) \frac{1}{|z|} [1 - \exp(-p|z|)] - q|z| \exp(-p|z|)$.

Here p and q are adjustable parameters. The solutions to the Schrödinger equation can then be written as a linear combination of the solutions in limiting cases of long chain length ($l = \infty$) and short chain length ($l \ll a_B$, where a_B is the effective Bohr radius):

$$\psi(z_e, z_h) = \alpha \phi(z_e) \phi(-z_h) + \beta A \sin\left(\frac{\pi z_e}{l}\right) \sin\left(\frac{\pi z_h}{l}\right) \times \tilde{\phi}(z_e, z_h) \quad (13)$$

where the term with α coefficient is the short chain solution and the term with β coefficient is the long chain solution⁵. From Equations 10-13, the expectation value

for the exciton energy can be calculated for varying chain lengths and agrees excellently with both more expensive computational techniques and experiment⁵.

IV. CONCLUSION

Hermitian operators are operators which satisfy the relation $\int \phi(\hat{A}\psi)^* d\tau = \int \psi^*(\hat{A}\phi) d\tau$ for any two well behaved functions. Hermitian operators play an integral role in quantum mechanics due to two of their properties. First, their eigenvalues are always real. This is important because their eigenvalues correspond to physical properties of a system, which cannot be imaginary or complex. Second, their eigenfunctions are orthonormal, which greatly simplifies many quantum mechanical problems.

The 1D PB model provides a simple illustration of the use Hermitian operators in solving quantum mechanical problems. Furthermore, this model can also be used to approximate electron excitations in cyanine dyes to an accuracy of a few percent⁴. The model can also be elaborated upon to accurately predict the exciton energies of conjugated polymers with markedly reduced computational time compared to other methods⁵.

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