

13 Theory of Operators: II

1. Representing operators

- (a) Earlier in the class we spoke about how we could “represent” vectors. That is any vector can be represented as a linear combination of a complete set of vectors. (If this statement is not clear, please revise Section 4 and also look through the Pauli Spin matrix homework and handout where we learnt how to represent the spin operators using the kets $|SG_z^+\rangle$ and $|SG_z^-\rangle$.)
- (b) Operators can be represented in a similar for. In fact if you have a complete set of vectors $\{|i\rangle\}$, we can write an operator as a matrix. What we mean by this is we could represent an operator using a collection of matrix elements that have the following form:

$$A_{j,l} \equiv \langle j | \hat{A} | l \rangle \quad (13.1)$$

$A_{j,l}$ is the (j, l) -th element of the matrix that is used to represent the operator \hat{A} . (Make sure to compare this with the Pauli spin matrix homework so you understand whats going on clearly.)

- (c) Does this definition make sense? $\hat{A} | l \rangle$ is another vector. You could call it $|m\rangle$ if you like. In that case the right hand side of Eq. (13.1) is the “dot” product of two vectors: $\langle j |$ and $|m\rangle$. The “dot” product of two vectors is a number. Hence the definition in Eq. (13.1) makes sense. (If these arguments are not a 100% clear to you, you need to go back and revise Section 4 and the related appendix.)

(d) For Eq. (13.1) to be useful we should know what \hat{A} does to $|l\rangle$ when it acts on it.

2. Lets now consider the individual parts of the Hamiltonian as seen in the description of the time-dependent and time-independent Schrödinger Equation. Here we will discuss representations for the Hamiltonian.

(a) The kinetic energy operator for the Hamiltonian is the second derivative operator. What we really did before we obtained the differential equation for the time-independent Schrödinger Equation for the particle in a box case is the following:

$$H |\psi\rangle = E |\psi\rangle \quad (13.2)$$

(b) We wrote this equation in the coordinate representation:

$$\begin{aligned} H \int dx |x\rangle \langle x | \psi\rangle &= E |\psi\rangle \\ \langle x' | K + V \int dx |x\rangle \langle x | \psi\rangle &= E \langle x' | \psi\rangle \end{aligned} \quad (13.3)$$

$$\begin{aligned} \int dx \langle x' | K |x\rangle \langle x | \psi\rangle + \int dx \langle x' | V |x\rangle \langle x | \psi\rangle \\ = E \psi(x') \end{aligned} \quad (13.4)$$

Note we have used the definition: $\psi(x') \equiv \langle x' | \psi\rangle$ in the last equation above.

(c) Here we did something but never spoke about it. We implicitly made the assumption that

$$\langle x' | V |x\rangle = V(x) \delta_{x,x'}. \quad (13.5)$$

That is the potential energy does not depend on two points in space but only depends on one point.

- (d) Does this make sense? The classical definition of the potential energy is the energy due to the position of an object and hence it should depend only on one index x which is the position of the object. Such potential energies are called *local* potential energies. There exists a family of potential energies where we cannot make this simplification, that is we have to leave V as a function of two points as in the equation above and these are called *non-local* potentials. We will not see any *non-local* potentials in this course.
- (e) This assumption of local potentials reduced our equation to:

$$\int dx \langle x' | K | x \rangle \langle x | \psi \rangle + V(x)\psi(x) = E\psi(x') \quad (13.6)$$

The first on the left hand side is another way to write the second derivative operator and this is how we got our differential equation that we solved for the particle in a box and other one-dimensional problems.

- (f) The reason we are going through this digression is to realize that the matrix element of the operator we defined in Eq. (12.12) is something we implicitly used in writing down the differential equation. The differential equation had the corresponding form only because we chose to write the equation in the coordinate representation!! (We could have chosen any other complete set to write the Schrödinger Equation in and in such a case we would have needed the matrix elements in that basis set.)

3. Hermitian Operators

- (a) Do eigenvalues have to be real? No. a in Eq. (12.11) could be complex. But if a is a measurable quantity it would have to be real. Right?
- (b) What are the requirements that a has to be real?
- (c) It turns out a is real for a very special kind of operator. It is called the Hermitian operator. Before we introduce a Hermitian operator it is required that we introduce the following concept: *the dual space analogue of an operator*.
- (d) The *the dual space analogue of an operator* \hat{A} is represented by the operator \hat{A}^\dagger . (Note this is the same notation we used for vectors.) This matrix is defined in the following fashion:

$$\langle j | \hat{A}^\dagger | l \rangle = \langle l | \hat{A} | j \rangle^* \quad (13.7)$$

Does this definition make sense?

- (e) A Hermitian operator is define as an operator that satisfies:

$$\hat{A}^\dagger = \hat{A}. \quad (13.8)$$

That is:

$$\langle j | \hat{A} | l \rangle = \langle l | \hat{A} | j \rangle^* \quad (13.9)$$

Note the left hand is $A_{(j,l)}$ and the right hand side is $A_{(j,l)}^\dagger$, hence when we say that the two operators are equal we require that every element of the corresponding matrices are equal.

- (f) Examples of Hermitian operators. The potential energy operator and the momentum operator are examples of Hermitian operators. For the potential energy operator:

$$\begin{aligned}\langle j | V | l \rangle &= \langle j | \int dx |x\rangle \langle x| V \int dx' |x'\rangle \langle x'| |l\rangle \\ &= \int dx \int dx' \langle j | |x\rangle \langle x| V |x'\rangle \langle x'| |l\rangle \\ &= \int dx \int dx' j(x)^* V(x) \delta_{x,x'} l(x') \quad (13.10)\end{aligned}$$

The requirement of *local* potential makes x and x' the same and we get:

$$\langle j | V | l \rangle = \int dx j(x)^* V(x) l(x) \quad (13.11)$$

We can similarly write the right hand side of Eq. (13.9) as

$$\begin{aligned}[\langle l | V | j \rangle]^* &= \left[\int dx l(x)^* V(x) j(x) \right]^* \\ &= \int dx l(x) V(x)^* j(x)^* \\ &= \int dx l(x) V(x) j(x)^* \\ &= \langle j | V | l \rangle \quad (13.12)\end{aligned}$$

Hence, if the potential energy is real over all space (which it is *in many physical problems*), the potential energy operator is Hermitian

For the momentum operator:

$$\begin{aligned}
 \langle j | \hat{p} | l \rangle &= \langle j | \int dx | x \rangle \langle x | \hat{p} \int dx' | x' \rangle \langle x' | | l \rangle \\
 &= \int dx \int dx' \langle j | | x \rangle \langle x | \hat{p} | x' \rangle \langle x' | | l \rangle \\
 &= \int dx \int dx' j(x)^* \left[-i\hbar \frac{\partial}{\partial x} \right] \delta_{x,x'} l(x') \quad (13.13)
 \end{aligned}$$

This gives

$$\begin{aligned}
 \left\langle j \left| \left[-i\hbar \frac{\partial}{\partial x} \right] \right| l \right\rangle &= -i\hbar \int dx j(x)^* \frac{\partial}{\partial x} l(x) \\
 &= -i\hbar j(x)^* l(x) \Big|_{x \rightarrow -\infty}^{x \rightarrow +\infty} \\
 &\quad + i\hbar \int dx \frac{\partial j(x)^*}{\partial x} l(x) \quad (13.14)
 \end{aligned}$$

Now we require that the functions $j(x)$ and $l(x)$ be normalizable. For this to be true $j(x)$ and $l(x)$ must go to zero at $\pm\infty$. (Note that this argument is different from the argument you saw in the extra-credit homework last week on the finite Fourier transform of the time-dependent SE.)²

$$\begin{aligned}
 \left\langle j \left| \left[-i\hbar \frac{\partial}{\partial x} \right] \right| l \right\rangle &= \int dx \left[-i\hbar \frac{\partial j(x)}{\partial x} \right]^* l(x) \\
 &= \left\{ \int dx \left[-i\hbar \frac{\partial j(x)}{\partial x} \right] l(x)^* \right\}^* \\
 &= \left\langle l \left| \left[-i\hbar \frac{\partial}{\partial x} \right] \right| j \right\rangle^* \quad (13.15)
 \end{aligned}$$

Hence the momentum operator is Hermitian.

Homework: Using the same approach as above, show that the kinetic energy operator is Hermitian.

Hence the Hamiltonian operator is a Hermitian operator.

²Functions that are normalizable are called quadratically integrable functions.

(g) **A Hermitian operator always has real eigenvalues** Consider the eigenvalue problem for the Hermitian operator \hat{A} :

$$\hat{A} |\eta\rangle = a |\eta\rangle \quad (13.16)$$

Left-multiplying both sides by $\langle\eta|$ and noting that $\langle\eta| \eta\rangle = 1$:

$$\langle\eta| \hat{A} |\eta\rangle = a \quad (13.17)$$

Now consider the complex conjugate of the above equation:

$$\{\langle\eta| \hat{A} |\eta\rangle\}^* = a^* \quad (13.18)$$

Since \hat{A} is a Hermitian operator, the left side of Eq. (13.17) and Eq. (13.18) are equal:

$$\langle\eta| \hat{A} |\eta\rangle = \{\langle\eta| \hat{A} |\eta\rangle\}^* \quad (13.19)$$

Note that this is a special case of Eq. (13.9). Hence the left side of Eq. (13.17) and Eq. (13.18) should also be equal. That is,

$$a^* = a \quad (13.20)$$

But this can only be true if a is real.

Hence the eigenvalues of a Hermitian operator are always real.

Since we associate operators with observable quantities, and since quantities we observe must be real, this property is extremely powerful. *It means that most operators that are associated with observable quantities must be Hermitian operators, and hence have real eigenvalues.* Thus the fact that the Hamiltonian is a Hermitian operator comes as no surprise since the energy is a real observable quantity!! Such is also the case for the momentum operator.

(h) **The eigenvectors of a Hermitian operator are orthogonal** Let $|j\rangle$ and $|l\rangle$ above be two specific eigenvectors of the Hermitian operator \hat{A} . Then it must be true that

$$\begin{aligned}\hat{A}|j\rangle &= a_j|j\rangle \\ \hat{A}|l\rangle &= a_l|l\rangle\end{aligned}\quad (13.21)$$

Now consider the property of the Hermitian operator \hat{A} :

$$\langle j|\hat{A}|l\rangle = \langle l|\hat{A}|j\rangle^* \quad (13.22)$$

Since $|j\rangle$ and $|l\rangle$ are eigenvectors of \hat{A}

$$\langle j|a_l|l\rangle = \langle l|a_j|j\rangle^* \quad (13.23)$$

That is,

$$\begin{aligned}a_l\langle j||l\rangle &= a_j^*\langle l|j\rangle^* \\ &= a_j\langle l|j\rangle^*\end{aligned}\quad (13.24)$$

Where the last statement is true because a_j has to be real as seen earlier.

Now since $a_l \neq a_j$ in general, since any two arbitrary eigenvectors of \hat{A} don't in general have the same eigenvalues, It must be required that

$$\langle l|j\rangle = 0 \quad (13.25)$$

Hence the non-degenerate eigenvectors of a Hermitian operator are orthogonal.

Degenerate eigenvectors, in general, need not be orthogonal but it is possible to construct orthogonal vectors from any two degenerate eigenvectors.

Homework: We will now prove the last statement

- i. Consider two *normalized* vectors \vec{a} and \vec{b} . Let these not be orthogonal. That is,

$$\vec{a} \cdot \vec{b} = N \neq 0. \quad (13.26)$$

Where N is a number that is non-zero. Does this equation make sense? Remember, we learned earlier that two vectors are orthogonal if their “dot” product is zero. Please revise Section 4, A and B. Here the vectors \vec{a} and \vec{b} are not orthogonal.

- ii. Consider the vector:

$$\vec{c} = \vec{a} - N\vec{b} \quad (13.27)$$

Show that the vector \vec{c} is orthogonal to the vector \vec{b} .

- iii. Interpret Eq. (13.27) in a physical fashion. (Note: To do this you will need to remind your self what a “dot” product really means.)
- iv. The Eq. (13.27) shows that we can construct a vector from \vec{a} that is orthogonal to \vec{b} .
- v. Eq. (13.27) is called the Gram Schmidt orthogonalization scheme and is very commonly used in quantum chemistry.
- vi. This procedure can be generalized to more than two degenerate set of vectors.

4. To summarize: Hermitian operators have the following two very important properties:

- (a) *Hence the eigenvalues of a Hermitian operator are always real.* This allows us to write all observables in terms of operators that are Hermitian. This is true for the energy (Hamiltonian), the momentum, spin, and many other operators that we will come across
- (b) *The eigenvectors of a Hermitian operator are orthogonal.* This is also a powerful statement. In fact the eigenstates of a Hermitian operator are orthogonal *and complete*. This means that any *ket*-vector can be written as a linear combination of a set of eigenvectors of a Hermitian operators. What does this mean? Say you have an oxygen atom and a hydrogen atom. And say you have solved the Schrödinger Equation for both these atoms. This means you know the eigenvectors of oxygen and the eigenvectors of hydrogen. (*The eigenvectors are what we chemists call orbitals!!*) Since the Hamiltonian for the oxygen atom and the Hamiltonian for the hydrogen atom are Hermitian operators, it must be true that these set of eigenvectors form a complete set!! So now lets say we want to solve for the eigenvectors of a water molecule (that is two hydrogens and one oxygen!!) We can use the eigenvectors of the single hydrogen and oxygen atoms as *basis-vectors* to solve the problem for water!!! This would be convenient, because we have already solved part of the problem. In fact such, approaches are used every day in quantum chemistry to simplify problems.

To further understand this discussion, please remind yourself that we solved the particle in a box problem and other one-dimensional problems earlier using the *coordinate representation*. (Do we remember what the coordinate representation is? Revise Section 4.3.1 and other related sections.) Here we are proposing an approach where we can use a different representation, a representation that comprises eigenstates of problems we solved earlier (the H and O atoms) to solve a more complicated problem H_2O .