Eigenvalue Equations

1. What is an eigenvalue equation?

First, here is a general definition applicable to functions of one variable x. Let $\hat{O}$ be an operator which operates on functions of x. Let's denote the *eigenfunctions* of $\hat{O}$ as $f_j(x)$, or collectively as $\{f_j(x)\}$ — the set of functions $f_j(x), j = 1, 2, 3, \ldots$; and let's denote the *eigenvalues* of $\hat{O}$ as λ_j or collectively as $\{\lambda_j\}$. Suppose we *know* $\hat{O}$: by definition, we get the eigenfunctions and eigenvalues $(f_j(x), \lambda_j)$ of $\hat{O}$ by solving the equation

$$\hat{O}\, f(x) \;=\; \lambda\, f(x) \tag{1}$$

Note that each eigenfunction $f_j(x)$ has *one* eigenvalue λ_j associted with it, ie, eigenfunctions and eigenvalues come in pairs $(f_j(x), \lambda_j)$. Typically, there are many solutions to this equation: $(f_1(x), \lambda_1)$, $(f_2(x), \lambda_2)$, $(f_3(x), \lambda_3)$, ... In QM we often encounter operators whose eigenvalue equation has *infinitely many* solutions.

2. Examples of operators and their eigenvalue equation.

The first example $\hat{D} = \frac{d^2}{dx^2}$. If we substitute this operator in equation (1), we see the solutions are functions $f(x)$ which have this property: if you differentiate $f(x)$ twice, you get back $f(x)$ to within a constant. Exponentials, cosine, and sine functions fit that description, so the solutions will have the form Ce^{ax}, $C\sin(ax)$, $C\cos(ax)$, where C and a could be any number, real or complex. The eigenvalues associated with these functions are as follows: (Ce^{ax}, a^2) ; $(C\sin(ax), -a^2)$; $(C\cos(ax), -a^2)$.

The second example is an operator $\hat{T}$ whose effect is to transform the function $f(x)$ into $f(3x)$, ie, it triples the argument of the function. In this case, the (eigenfunction, eigenvalue) pairs that are solution of equation (1) are: $(Cx^n, 3^n)$. For instance, if we substitute the function $f(x) = 5 \cdot x^4$ into equation (1), with

the operator $\hat{T}$:

$$\hat{T}\,5\cdot x^4 \;=\; 5\cdot(3x)^4 = 81\cdot(5x^4) = 3^4\cdot(5x^4)$$

which shows that $f(x) = 5\cdot x^4$ is indeed an eigenfunction of $\hat{T}$ with the associated eigenvalue 81.
The third example is a "reflection operator" $\hat{R}$: the effect of $\hat{R}$ on any function of $f(x)$ is to change its argument x to $-x$. The (eigenfunction, eigenvalue) solutions are $(Cx^n, -1^n)$. For example:

$$\begin{aligned}
\hat{R}\,x &= -x = (-1)\,x \\
\hat{R}\,x^2 &= (-x)^2 = (+1)\,x^2 \\
\hat{R}\,x^3 &= (-x)^3 = (-1)\,x^3 \\
\hat{R}\,x^4 &= (-x)^4 = (+1)\,x^4 \\
&\text{etc.}
\end{aligned}$$

3. What is the role of eigenvalue equation in quantum mechanics?

The Schrödinger equation is the basic equation for obtaining the constant energy states of atoms, molecules, etc. The Schrödinger equation itself is an eigenvalue equation. In its general form, it is

$$\hat{H}\,\psi \;=\; E\,\psi \tag{2}$$

The rules for obtaining the kinetic and potential energy parts of $\hat{H}$ are given in Silbey Equation (9.17) and Table 9.1. Understanding eigenvalue equations, in general, is useful for understanding the Schrödinger equation, its solutions, and the implications for chemistry. Note that the functions in the first example (exponentials, sines, cosines and their eigenvalues) were only an *intermediate result* in solving the Schrödinger equation for the particle in a box (PIB). In addition to solving the general eigenvalue equation, one uses physical arguments to find which functions make sense physically. In the case of the PIB, we could not take just any exponential, sine, or cosine function: the function we were looking for had to be a solution of the eigenvalue equation *and also had to be*

zero at $x = 0$ and $x = a$ (the positions of the left and right walls of the box). This is an example of a *boundary condition*. A boundary condition is something we know about a specific system (for ex., $f(a) = 0$ for the PIB) in addition to Schrödinger's equation. Boundary conditions give additional equations, on top of Schrödinger's equation, and this "narrows down" the number of acceptable wavefunctions. For example, for the PIB, it leads to sine functions with quantized wavelengths and quantized energies (Equation (9.67), (9.63)), not just any sine function.

Eigenvalue equations are even more important than the Schrödinger equation would suggest. One of the postulates (or "axioms") of quantum mechanics — Postulate 2 on page 336 of Silbey — is that to each physical property (energy, momentum, position, kinetic energy, number of particles, etc.) there is an associated *operator*: see again Table 9.1. Further, Postulate 3 (also on page 336) says that the result of **a measurement of that property must give one of the eigenvalues associated with that operator**.

There are two other essential ideas relating to operators and their eigenfunctions. Suppose $\hat{O}$ denotes a QM linear operator for a system of particles, and $\{\phi_j, \lambda_j\}$ is the set of all its eigenfunction-eigenvalue pairs. Then:

- ϕ_j and ϕ_k $(j \neq k)$ are orthogonal, meaning $\int \phi_j^* \phi_k \, d\tau = 0$.
- Any wavefunction ψ for the same system of particles can be written as a linear combination of the eigenfunctions:
$$\psi = \sum_j c_j \phi_j$$

4. Eigenvalues of operators and measurements.

To clarify the relation between the eigenvalues of an operator $\hat{A}$ and measurments of the property A, here are some examples.

First, suppose a H atom is in the $2s$ state. The wavefunction for that state is denoted ψ_{2s}. It is an eigenfunction of the hamiltonian $\hat{H}$ (energy operator) of the H atom. So we have this relation,

$$\hat{H}\,\psi_{2s} \;=\; E_{2s}\,\psi_{2s}$$

ie, an eigenvalue equation. If we measure the energy of a H atom initially in the ψ_{2s} state, we are sure to get E_{2s} as the result.

As a second example, suppose the H atom is initially in the $2s$ state as before, but now we measure the x compoment of momentum $\hat{p}_x$ of the electron. What are we going to get? To find out, we have to solve another eigenvalue equation, the one for the momentum operator. We write this equation symbolically

$$\hat{p}_x \, \phi_k \;\; = \;\; p_{x,k} \, \phi_k$$

I will not show the solutions to this equation, but assume we know them, ie, assume we know the $p_{x,k}$'s and ϕ_k's. Here's a crucial point: the function ψ_{2s} is *not* one of the ϕ_k's. Because of that, we can not tell with any certainty what result we are going to get when we measure p_x for a H atom initially in state ψ_{2s}. All we can say is that we are going to get one of the $p_{x,k}$ values, because *they* are the eigenvalues of $\hat{p}_x$. What we *can* predict is the *average value* $< p_x >$ of many measurements of p_x. This is going to be

$$< p_x > \;\; = \;\; \int \psi^*_{2s} \, \hat{p}_x \, \psi_{2s} \, d\tau$$

where I used a short-hand notation to represent a 3-dimensional integral over all space. Note that the operators $\hat{H}$ and $\hat{p}_x$ do not commute: this implies that we can not measure simultaneously the energy and p_x with perfect precision. When the H atom is initially in the $2s$ state, we can measure its energy with perfect precision (and the result of the measurement is prefectly predictable, it is E_{2s}) but we can not measure at the same time p_x with any kind of precision (the result of any *single* measurement of p_x is totally unpredictable). Note also that, when the H atom is initially in the $2s$ state, the average value of the energy over many measurements is obviously E_{2s}: in fact, *each and every energy measurement gives* E_{2s}, as stated in the first example. We can write an equation to show this:

$$\begin{aligned} < E > \;\; &= \;\; \int \psi^*_{2s} \, \hat{H} \, \psi_{2s} \, d\tau \\ &= \;\; \int \psi^*_{2s} \, E_{2s} \, \psi_{2s} \, d\tau \\ &= \;\; E_{2s} \cdot \int \psi^*_{2s} \, \psi_{2s} \, d\tau \\ &= \;\; E_{2s} \cdot 1 = E_{2s} \end{aligned}$$

Could we have a third case where the H atom is initially in a state ϕ_m, where ϕ_m is an eigenfunction of $\hat{p}_x$? Sure we could. In *that situation*, measuring the x component of momentum would give the result $p_{x,m}$ with certainty (100% probability), and measuring the energy would give a totally unpredictable result. As in the previous paragraph, we would only be able to calculate the *average energy* for a very large number of measurements each done from the initial state ϕ_m.

Finally, it is also entirely possible that a H atom would be in a state ψ' that is *neither* an eigenfunction of $\hat{H}$ or $\hat{p}_x$. In that case, we can not predict with any certainty the result of a measurement of energy, or of a measurement of p_x. We could still calculate the average value of very many measurements all done with the initial state ψ' with the formulas

$$< E > = \int \psi'^* \hat{H} \psi' \, d\tau$$

$$< p_x > = \int \psi'^* \hat{p}_x \psi' \, d\tau$$

5. Where do all these relations between operator and property, eigenvalue and measurement, come from?

This is a tough question best left for upper level courses. Here we can give two simple answers that are not fully satisfactory.

(1) If you look back at section 9.3, you will see that the Schrödinger equation was obtained by carrying the analogy between waves and particles and taking a "leap of faith": one assumes that matter obeys the same wave equation as in classical mechanics, except that we replace the wavelength λ (in equation 9.14) by the de Broglie expression. By doing that, you effectively construct the quantum mechanical energy operator $\hat{H}$ and establish its relation to energy measurements.

(2) Or, one could simply say that the postulates 1–6 (pages 336, 337) state the relation between eigenvalue equations and values we get when we measure

properties. Postulate can't be proven, they have to be accepted or rejected. But once a set of postulates is accepted as a working hypothesis, one can derive equations and make predictions about experiments. So far, the predictions of QM theory agree with all experimental results that fall within the scope of QM: that is a strong argument for believing that the postulates are "true".