

Notes on Derivation and Features of the Time Independent Schrödinger Equation (TISE)

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Massachusetts Institute of Technology

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So far we have built the following items into our theory: quantum states and superposition, the interpretation of the magnitude squared of quantum amplitudes as probabilities, both de Broglie Hypothesis and the notion of quantum determinism.

As partial verification, out of our theory we have recovered the following new physical facts which were not built directly into the theory, the Heisenberg uncertainty principle, the conservation of probabilities and the correspondence principle (Ehrenfest's theorem).

We now enter the next phase of the course where we will use our formalism to predict new phenomena. To make these predictions, in principle all that one needs to know is the time dependent Schrödinger equation (TDSE) describing how our quantum states change in time and how to use the resulting wavefunctions to compute quantum probabilities and averages. All of the development you will see throughout the rest of this course follows directly from the TDSE.

However, the TDSE is a complicated partial differential equation. While (as in Problem Set 6) one may at times be able to “guess” at solutions to the Schrödinger equation, it is necessary to equip ourselves with a set of general mathematical tools for solving the TDSE. The purpose of this note is to give you the first tool in this arsenal, *the method of separation of variables*. With separation of variables you will be able to eliminate the time dependence from the TDSE and produce a new, time independent equation, the *Time Independent Schrödinger Equation* (TISE). For one dimensional systems, the TISE will no longer be a partial differential equation but will be an ordinary differential equation which is then much easier to solve.

After deriving the TISE, this note will go on to explore some of the general features of its solutions. We do this before we move on in the course to discuss methods to solve the TISE in specific instances. The first methods we will discuss for solving the TISE in one dimension will be the qualitative methods laid out in Section 3.11 of the text, *French and Taylor*.

1 Separation of Variables

The time dependent Schrödinger equation in a *three dimensional* system reads

$$i\hbar\partial_t\Psi(\vec{x}, t) = \hat{H}\Psi(\vec{x}, t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(\vec{x}, t) + V(\vec{x})\Psi(\vec{x}, t). \quad (1)$$

For a one dimensional system it becomes just

$$i\hbar\partial_t\Psi(x,t) = \hat{H}\Psi(x,t) = -\frac{\hbar^2}{2m}\partial_x^2\Psi(x,t) + V(x)\Psi(x,t). \quad (2)$$

As in the previous note, although we shall focus for the most part of this course on one dimensional systems, we shall carry through the developments in this note for the more general case of three dimensional systems which we *will* need when we study the hydrogen atom. To recover the one dimensional results, you need only remove the vector symbol “ $\vec{}$ ” and replace ∇ with ∂_x in all of the equations below.

The method of the separation of variables is most often applied in the case of linear partial differential equations. We would like to emphasize at this point that the TDSE is linear, which means that the sum of any two solutions $\Psi_1(\vec{x},t)$ and $\Psi_2(\vec{x},t)$ to the equation gives a third valid solution $\Psi_3(\vec{x},t) = \Psi_1(\vec{x},t) + \Psi_2(\vec{x},t)$. The student may verify this easily by direct substitution of $\Psi_3(\vec{x},t)$ into (1).

Note that in the equations below we have written the wave function, $\Psi(\vec{x},t)$ as with an *upper case* letter Ψ . We do this because momentarily we will separate the time and spatial dependencies of these equations and derive a new equation, the TISE, describing a time-independent wavefunction $\psi(\vec{x})$ which we will denote with a *lower case* ψ .

1.1 The separation procedure

To separate the spatial from time dependencies in the TDSE, we must assume that the potential $V(\vec{x})$ is constant *in time*. This will cover all of the cases of interest to us. It is valid for any isolated system. If some external influence acts on the system then V will have a time dependence, and more sophisticated procedures must then be employed to solve the TDSE.

We begin the separation procedure by noting that (for those V which are constant in time) all of the *operators* on the left hand side of (1) involve only the time variable t and none of the spatial variables \vec{x} , whereas all of the *operators* on the right hand side involve the spatial variables \vec{x} only. The only appearance of spatial variables on the left hand side is as arguments to the wave function and the only appearance of the time variable on right hand side is also as an argument to the wave function. We could separate the dependencies in the equation entirely if we could only break up the variable dependencies in $\Psi(\vec{x},t)$. This observation leads us to seek solutions to (1) of the separated form

$$\Psi(\vec{x},t) = \psi(\vec{x})\phi(t) \quad (3)$$

Substituting this *ansatz* (guess) into (1) gives

$$\begin{aligned} i\hbar\partial_t\psi(\vec{x})\phi(t) &= \hat{H}\psi(\vec{x})\phi(t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x})\phi(t) + V(\vec{x})\psi(\vec{x})\phi(t) \\ \psi(\vec{x})i\hbar\partial_t\phi(t) &= \phi(t)\left(-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x})\right) + \phi(t)V(\vec{x})\psi(\vec{x}) \\ \psi(\vec{x})i\hbar\partial_t\phi(t) &= \phi(t)\left(-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{x}) + V(\vec{x})\psi(\vec{x})\right). \end{aligned}$$

Finally, dividing both sides by $\Psi(\vec{x},t) = \psi(\vec{x})\phi(t)$,

$$i\hbar\frac{\partial_t\phi(t)}{\phi(t)} = \left(-\frac{\hbar^2}{2m}\frac{\nabla^2\psi(\vec{x})}{\psi(\vec{x})}\right) + V(\vec{x}). \quad (4)$$

In (4), the variables are now *completely* separated. Nothing on the left hand side depends on the spatial variables \vec{x} and nothing on the right hand side depends on the time variable t . Therefore, if the left hand side is to equal the right hand side for all \vec{x} and t , the two sides must both equal

something which depends on *neither* \vec{x} nor t . If we call this constant, which is independent of \vec{x} and t , E ,

$$E = i\hbar \frac{\partial_t \phi(t)}{\phi(t)} = \left(-\frac{\hbar^2}{2m} \frac{\nabla^2 \psi(\vec{x})}{\psi(\vec{x})} \right) + V(\vec{x}),$$

we now have two separate equations, one for ϕ

$$i\hbar \partial_t \phi(t) = E\phi(t), \quad (5)$$

and one for $\psi(\vec{x})$,

$$-\frac{\hbar^2}{2m} \nabla^2 \psi(\vec{x}) + V(\vec{x})\psi(\vec{x}) = E\psi(\vec{x}). \quad (6)$$

(We chose the letter E for this constant because it will later turn out to be the energy of the quantum state $\psi(\vec{x})\phi(t)$.)

(5) is a simple differential equation easily solved for the time dependent part $\phi(t)$,

$$\begin{aligned} i\hbar \partial_t \phi(t) &= E\phi(t) \\ i\hbar \frac{d\phi}{dt} &= E\phi \\ i\hbar \int \frac{d\phi}{\phi} &= \int E dt \\ i\hbar \ln \phi &= Et + C' \\ \phi &= e^{C'/i\hbar} e^{-iEt/\hbar} \\ \phi(t) &= C e^{-iEt/\hbar}. \end{aligned} \quad (7)$$

(6) is the Time Independent Schrödinger Equation for $\psi(\vec{x})$. At this point we have identified a whole *series* of solutions because generally there will be multiple values of the constant E for which (6) has solutions for $\psi(\vec{x})$. To distinguish the different solutions, we shall refer to them as $\psi_n(\vec{x})$ and call the corresponding values of E in (6) E_n . It will be true for most of the systems we shall study that the allowed values of E form a discrete set, as the notation E_n suggests. There are exceptions where there is a continuous range of allowed values of E . All of the developments below will still hold so long as summations over the discrete index n are replaced by appropriate integrations.

By the method of separation of variables, we have now identified a whole series of solutions to the TDSE of the form

$$\Psi_n(\vec{x}, t) = \psi_n(\vec{x}) e^{-iE_n t/\hbar}, \quad (8)$$

where

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n(\vec{x}) + V(\vec{x})\psi_n(\vec{x}) = E_n \psi_n(\vec{x}). \quad (9)$$

(We have absorbed the integration constant C from the solution to $\phi(t)$ into the function $\psi(\vec{x})$, a valid procedure because the TISE which $\psi(\vec{x})$ satisfies is linear and so multiplying $\psi(\vec{x})$ by a constant factor C has no effect on its validity as a solution.)

1.2 Completeness of the solution set: energy eigenstates, general solution to the TDSE

The intriguing thing about the solutions $\Psi_n(\vec{x}, t)$ of the previous section is that they form a *complete* set, which means that *all* valid solutions to (1) maybe made out of sums of the particular solutions Ψ_n we have identified. This is a general feature of the solutions generated by the procedure of the separation of variables. The proof of this as a *mathematical* statement is beyond the scope of

this course. We can see, however, on physical grounds that the solutions we have identified must be complete provided that we have the correct *mathematical* representation of our pure *physical* quantum states.

The physical reason for our confidence in the completeness of our solutions comes from the very special form of equation (9). It is just the eigenvalue equation for the energy operator!

$$-\frac{\hbar^2}{2m}\nabla^2\psi_n(\vec{x}) + V(\vec{x})\psi_n(\vec{x}) = \hat{H}\psi_n(\vec{x}) = E_n\psi_n(\vec{x}). \quad (10)$$

The ψ_n are eigenstates of the Hamiltonian operator \hat{H} . Each solution $\psi_n(\vec{x})$ to this equation is a pure state of the energy observable with energy E_n . The only values which may be observed when the measure the energy of the system are the E_n where (10) has a valid solution. This is the reason for our choice of the name E for the constant which appeared in our separation of variables analysis.

The completeness of our solutions may be understood through the physical principle of superposition, which states that we may write *all* quantum states at a given time $t = 0$ as an amplitude-weighted sum of the pure states of the physical observable of the energy,

$$|\Psi(t = 0)\rangle = \sum_n c_n |E_n\rangle. \quad (11)$$

In the position representation, this means that we may expand *any* wavefunction $\Psi(\vec{x}, t = 0)$ at time $t = 0$ in terms of our solutions to the TISE $\psi_n(\vec{x})$,

$$\Psi(\vec{x}, t = 0) = \sum_n c_n \psi_n(\vec{x}). \quad (12)$$

From our separation of variables, we do know that $\psi_n(\vec{x})e^{-iE_n t/\hbar}$ is a solution to the Time Dependent Schrödinger Equation (1). Because the TDSE is linear, $\sum_n c_n \psi_n(\vec{x})e^{-iE_n t/\hbar}$ is also a solution. Because, as we saw above, the c_n may be chosen so that $\sum_n c_n \psi_n(\vec{x})$ matches an arbitrary $\Psi(\vec{x}, t = 0)$ at $t = 0$, the general solution to the TDSE may be written

$$\Psi(\vec{x}, t) = \sum_n c_n \psi_n(\vec{x})e^{-iE_n t/\hbar}. \quad (13)$$

The interested student should note (and try as an exercise) that one may go (in three or four lines of algebra!) from the more abstract Schrödinger equation

$$i\hbar\partial_t|\Psi(t)\rangle = H_{op}|\Psi(t)\rangle$$

and the principle of superposition (11) to derive almost immediately the central result of this note (13).

2 Properties of Solutions of the TISE

While the TISE does represent a significant simplification over the full-blown TDSE, the TISE is itself a formidable equation. We have paid a price in the elimination in the time dependence from the equation describing $\Psi(\vec{x}, t)$. That price is the introduction of the unknown parameters E_n , the allowed “eigenenergies” of the system. While before we had a partial differential equation with an extra variable t , at least we knew at the start the values of all of the constants appearing in the TDSE (1). This is no longer the case with the TISE. We must somehow determine the values E_n . Before discussing methods for determining the allowed E_N and finding the solutions of the TISE, we will now discuss what we may say in general about these solutions. The first two facts we will discuss are general mathematical properties of the E_n the ψ_n respectively. The second two facts are more physical and give us insight into the allowed energies of a system, the E_n .

2.1 Realness of the eigenenergies E_n

While from their physical interpretation as the eigenvalues of a physical operator (10) and thus values observed in physical measurements, it is clear on *physical grounds* that the energy eigenvalues E_n must be real. Nonetheless, it is as useful exercise and a simple consistency check on our theory to *verify mathematically* that the eigenvalues of (10) are real. The mathematical proof follows directly from the Hermitianness of the energy operator \hat{H} . The proof we give below is completely general and can be applied to any Hermitian operator.

$$\begin{aligned}
 (\psi_n, \hat{H}\psi_n) &= (\hat{H}\psi_n, \psi_n) \quad ; \text{Hermitianness of } \hat{H} \\
 (\psi_n, E_n\psi_n) &= (E_n\psi_n, \psi_n) \quad ; \text{Def. of eigenvalue} \\
 E_n(\psi_n, \psi_n) &= E_n^*(\psi_n, \psi_n) \quad ; \text{Linearity properties of Hermitian inner product} \\
 E_n &= E_n^* \quad ; (\psi_n, \psi_n) \neq 0 \text{ unless } \psi_n = 0. \\
 \Rightarrow E_n &\text{ is real.}
 \end{aligned} \tag{14}$$

2.2 Orthogonality of the eigenstates $\psi_n(\vec{x})$ (Kronecker δ -function)

A useful property of the energy eigenstates $\psi_n(\vec{x})$ is that they are *orthogonal*, the inner product between the pure states associated with two different energies is always zero, $(\psi_n, \psi_m) = 0$. Again the proof we give is completely general and is valid for any Hermitian operator.

$$\begin{aligned}
 (\psi_n, \hat{H}\psi_m) &= (\hat{H}\psi_n, \psi_m) \quad ; \text{Hermitianness of } \hat{H} \\
 (\psi_n, E_m\psi_m) &= (E_n\psi_n, \psi_m) \quad ; \text{Def. of eigenvalue} \\
 E_m(\psi_n, \psi_m) &= E_n^*(\psi_n, \psi_m) \quad ; \text{Linearity properties of Hermitian inner product} \\
 E_m(\psi_n, \psi_m) &= E_n(\psi_n, \psi_m) \quad ; \text{realness of eigenvalues of Hermitian operator} \\
 (E_m - E_n)(\psi_n, \psi_m) &= 0 \\
 \Rightarrow (\psi_n, \psi_m) &= 0 \quad \text{if } E_n \neq E_m.
 \end{aligned} \tag{15}$$

If we agree to normalize our eigenstates properly so that $1 = \int \mathcal{P}_n(\vec{x}) d^3x = \iiint \psi_n^*(\vec{x})\psi_n(\vec{x}) d^3x \equiv (\psi_n, \psi_n)$, we then may write compactly

$$(\psi_n, \psi_m) = \delta_{nm}, \tag{16}$$

where δ_{nm} is the *Kronecker δ -function*, which is defined as

$$\delta_{nm} = \begin{cases} 1 & n = m \\ 0 & n \neq m \end{cases}. \tag{17}$$

With this understood, the determination of the constants c_n in the general expansion $\Phi(\vec{x}) = \sum_n c_n \psi_n(\vec{x})$ is now simple. To extract c_m , we just take the inner product of ψ_m with Φ ,

$$\begin{aligned}
 (\psi_m, \Phi) &= (\psi_m, \sum_n c_n \psi_n) \\
 &= \sum_n c_n (\psi_m, \psi_n) \quad ; \text{linearity property of the Hermitian inner product} \\
 &= \sum_n c_n \delta_{nm} \\
 &= c_m \\
 \Rightarrow c_m &= (\psi_m, \Phi).
 \end{aligned} \tag{18}$$

$$\tag{19}$$

With the c_m we now may compute the probabilities of measuring the value E_m in an experiment, $P_n = |c_n|^2$. We may also use them to give an explicit form for the expansion of an arbitrary state Φ in terms of the pure energy states ψ_m ,

$$\Phi(\vec{x}) = \sum_m \psi_m(\vec{x}) (\psi_m, \Phi) \tag{20}$$

2.3 Variational Principle

We now move to more physical statements about the behavior of the solutions of the TISE. The first of these is the variational principle.

In its simplest form, the variational principle is the mathematical expression of the physically sensible statement that the *average* energy observed for a system in any quantum state must be at least as large as the lowest energy state (ground state) of the system, E_0 . Despite its apparent simplicity, this principle is extremely powerful and forms the basis for the vast majority of large scale quantum calculations carried out in current research.

To express this principle mathematically, we begin with an arbitrary, not necessarily normalized wavefunction, $\Phi(\vec{x})$. To compute the average energy of the state described by $\Phi(\vec{x})$ we must first normalize Φ by dividing by the square root of the inner product of Φ with itself, $\frac{\Phi(x)}{\sqrt{(\Phi, \Phi)}}$. This function is now properly normalized

$$\left(\frac{\Phi}{\sqrt{(\Phi, \Phi)}}, \frac{\Phi}{\sqrt{(\Phi, \Phi)}}\right) = \frac{1}{\sqrt{(\Phi, \Phi)}} \cdot \frac{1}{\sqrt{(\Phi, \Phi)}} \cdot (\Phi, \Phi) = 1.$$

From the properly normalized state, we may compute the average energy,

$$\left(\frac{\Phi}{\sqrt{(\Phi, \Phi)}}, \hat{H} \frac{\Phi}{\sqrt{(\Phi, \Phi)}}\right) = \frac{1}{\sqrt{(\Phi, \Phi)}} \cdot \frac{1}{\sqrt{(\Phi, \Phi)}} \cdot (\Phi, \hat{H}\Phi) = \frac{(\Phi, \hat{H}\Phi)}{(\Phi, \Phi)}.$$

The quotient

$$\mathcal{R}[\Phi] = \frac{(\Phi, \hat{H}\Phi)}{(\Phi, \Phi)} \quad (21)$$

has a special name and is known as the *Rayleigh* quotient.

The variational principle states that the Rayleigh quotient is never be less than the ground state energy. Because the Rayleigh quotient takes on the value of the ground state energy when Φ is the ground state, the mathematical expression of the variational principle is the statement that the function $\mathcal{R}[\Phi]$ has its minimum at the ground state energy,

$$\min_{\Phi} \mathcal{R}[\Phi] = \min_{\Phi} \frac{(\Phi, \hat{H}\Phi)}{(\Phi, \Phi)} = E_0.$$

We shall prove an even more general version of this statement. The minimum of a function is just a special case of a critical or *stationary* point. A stationary point, like the minimum, is an input value in the domain of a function where all of the *first* derivatives of a function are zero. This means that if we move slightly away from a critical point, the value of the function changes only slightly and varies only to second order in the distance from the critical point. We refer to the nearly constant behavior of a function near a critical point by saying that the function is *stationary* about the critical points. We will now show that the variational principle:

Variational Principle: the Rayleigh quotient $\mathcal{R}[\Phi]$ is stationary about all of the eigenstates $\Phi = \psi_n$.

Phrased in this more general way, the variation principle may be used to help identify *excited* as well as ground states. We will see an example of how this principle may be used in the next section where we use it to prove an extremely general version of the virial theorem.

To prove the stationary property of the Rayleigh quotient, imagine that we are in the vicinity of one of the eigenstates ψ_n so that $\Phi = \psi_n + \phi$, where ϕ is relatively small. Using (20) we may decompose $\phi = \sum_m c_m \psi_m$, where because ϕ is small, the c_n will be small also. To prove that $\mathcal{R}[\Phi]$ is stationary about ψ_n we now just have to show that the Rayleigh quotient is nearly constant, $\mathcal{R}[\psi_n + \sum_m c_m \psi_m] = E_n$ to first order in the c_n .

We proceed by first expanding the denominator and then the numerator of $\mathcal{R}[\Phi]$, both to second order in the c_n . The expansion of the denominator is

$$\begin{aligned}
\left(\psi_n + \sum_m c_m \psi_m, \psi_n + \sum_l c_l \psi_l \right) &= (\psi_n, \psi_n) + \sum_l c_l (\psi_n, \psi_l) + \sum_m c_m^* (\psi_m, \psi_n) + \sum_{ml} c_m^* c_l (\psi_m, \psi_l) \\
&= \delta_{nn} + \sum_l c_l \delta_{nl} + \sum_m c_m^* \delta_{mn} + \sum_{ml} c_m^* c_l \delta_{ml} \\
&= 1 + c_n + c_n^* + \sum_l c_l^* c_l \\
&= (1 + c_n + c_n^*) + \sum_l |c_l|^2
\end{aligned}$$

The expansion of the numerator is quite similar,

$$\begin{aligned}
\left(\psi_n + \sum_m c_m \psi_m, \hat{H}(\psi_n + \sum_l c_l \psi_l) \right) &= \left(\psi_n + \sum_m c_m \psi_m, E_n \psi_n + \sum_l c_l E_l \psi_l \right) \\
&= E_n (\psi_n, \psi_n) + \sum_l E_l c_l (\psi_n, \psi_l) + \sum_m E_n c_m^* (\psi_m, \psi_n) + \sum_{ml} E_l c_m^* c_l (\psi_m, \psi_l) \\
&= E_n \delta_{nn} + \sum_l E_l c_l \delta_{nl} + \sum_m E_n c_m^* \delta_{mn} + \sum_{ml} E_l c_m^* c_l \delta_{ml} \\
&= E_n + E_n c_n + E_n c_n^* + \sum_l E_l c_l^* c_l \\
&= E_n (1 + c_n + c_n^*) + \sum_l E_l |c_l|^2
\end{aligned}$$

Finally, we combine our two results

$$\begin{aligned}
\mathcal{R}[\Phi] &= \frac{(\Phi, \hat{H}\Phi)}{(\Phi, \Phi)} \\
&= \frac{E_n (1 + c_n + c_n^*) + \sum_l E_l |c_l|^2}{(1 + c_n + c_n^*) + \sum_l |c_l|^2} \\
&= \frac{E_n + \sum_l E_l \frac{|c_l|^2}{1 + c_n + c_n^*}}{1 + \sum_l \frac{|c_l|^2}{1 + c_n + c_n^*}} \\
&= \frac{E_n + \sum_l E_l |c_l|^2}{1 + \sum_l |c_l|^2} + \mathcal{O}(c^3) \quad (\text{correct to second order in the } c\text{'s}) \\
&= \left(E_n + \sum_l E_l |c_l|^2 \right) \left(1 - \sum_l |c_l|^2 \right) + \mathcal{O}(c^3) \\
&= E_n + \sum_l E_l |c_l|^2 - E_n \sum_l |c_l|^2 + \mathcal{O}(c^3) \\
&= E_n + \sum_l (E_l - E_n) |c_l|^2 + \mathcal{O}(c^3).
\end{aligned}$$

Here we have kept our expression correct up to and including second order terms in the c 's, lumping all third *and higher* order terms together in $\mathcal{O}(c^3)$. We see that there are no correction terms first order in the c 's. $\mathcal{R}[\Phi]$ is therefore stationary about the value E_n , which is what we had wanted to prove. Moreover, we immediately see that $E_l - E_n \geq 0$ if $n = 0$ is the ground state, and thus the corrections are always positive near the ground state. Thus we also see that $\mathcal{R}[\psi_0]$ is a minimum about the ground state as promised.

2.4 Virial Theorem

Aside from its value in computer calculations, the variational principle is a very powerful theoretical tool. It allows us to prove an extremely general result, the Virial theorem, regarding the averages of the various terms in the energies for systems in pure energy states. In its most general form, the Virial theorem is true even for systems containing of many particles such as macroscopic objects.

The virial theorem states that if the potential energy function $V(\vec{x}_1, \dots, \vec{x}_N)$ of a system of N particles is a homogeneous function of order v of the coordinates,

$$V(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N) = \lambda^v V(\vec{x}_1, \dots, \vec{x}_N),$$

then for each and every pure state n of the total energy operator \hat{H} of energy E_n the average kinetic energy $\langle T \rangle_n$ and average potential energy $\langle V \rangle_n$ of the system must obey

$$\langle T \rangle_n = \frac{v}{2} \langle V \rangle_n \quad (22)$$

$$\begin{aligned} \Rightarrow E_n &\equiv \langle T \rangle_n + \langle V \rangle_n \\ &= \frac{2+v}{2} \langle V \rangle_n \end{aligned} \quad (23)$$

$$= \frac{2+v}{v} \langle T \rangle_n . \quad (24)$$

Examples we have see so far of this are the simple harmonic oscillator $V(x) = \frac{1}{2}m\omega^2 x^2 \Rightarrow v = 2$, the Hydrogen atom $V(r) = e^2/r \Rightarrow v = -1$, and the bouncing ball $V(z) = mgz \Rightarrow v = 1$. We have also touched on a multiple particle system which fits into this framework as well, the multiple electron atom. In fact, any system composed of electrons and nuclei, such as *yourself*, satisfies the conditions of the virial theorem. By far the most important force in systems composed of electrons and nuclei is the electrostatic force. In the case of a single atom, if \vec{R} is the position of the nucleus of charge Z and $\{\vec{x}_i\}_{i=1}^Z$ are the positions of the Z electrons, then we have $N = Z + 1$ particles and $V(\vec{R}, \vec{x}_1, \dots, \vec{x}_Z) = \sum_{i=1}^Z \frac{-Ze^2}{|\vec{R}-\vec{x}_i|} + \sum_{i<j} \frac{e^2}{|\vec{x}_i-\vec{x}_j|}$. In this case and cases with more than one nuclei, V is still a homogeneous function of order $v = -1$.

In all of these cases, the virial theorem allows us to make *exact* quantum mechanical statements about the pure energy states of systems,

$$\langle T \rangle_n = -\frac{1}{2} \langle V \rangle_n, \quad (\text{Hydrogen Atom/Multiple Electron Atom/You})$$

$$\langle T \rangle_n = \langle V \rangle_n, \quad (\text{Simple Harmonic Oscillator})$$

$$\langle T \rangle_n = \frac{1}{2} \langle V \rangle_n . \quad (\text{Bouncing Ball}).$$

2.4.1 Preview of multiple particle systems

The formal part of this course deals almost exclusively with systems of one particle. While we have not yet discussed all the the physics of multiple particle systems, the general considerations we have laid out so far are sufficient for us to formulate and give a valid proof the virial theorem in the general case of more than one particle.

Within our framework, a systems of N particles is described by the coordinates of the particles in the system $\{\vec{x}_i\}_{i=1}^N$. Measurements of the positions of the particles in the system will lead to a distribution of results, where some probability function $\mathcal{P}(\vec{x}_1, \dots, \vec{x}_N) d^3x_1 \dots d^3x_N$ describes the probability of finding a particle in the small volume d^3x_1 around \vec{x}_1 and another particle in the volume d^3x_2 about \vec{x}_2 and so forth for all of N particles in the system. For a given quantum state $|\Psi\rangle$ of the system, this probability is given by the square of a quantum probability amplitude $\mathcal{P}(\vec{x}_1, \dots, \vec{x}_N) = |\Psi(\vec{x}_1, \dots, \vec{x}_N)|^2$. The wavefunction of the n^{th} pure state of energy will be an eigenstate of the Hamiltonian (total energy) operator,

$$\hat{H}\Psi_n(\vec{x}_1, \dots, \vec{x}_N) = E_n\Psi_n(\vec{x}_1, \dots, \vec{x}_N), \quad (25)$$

where the Hamiltonian \hat{H} is the sum of the total kinetic and potential energy operators,

$$\begin{aligned}\hat{H} &= \sum_{i=1}^N \frac{\hat{p}_i^2}{2m_i} + V(\hat{x}_1, \dots, \hat{x}_N) \\ &= \sum_{i=1}^N \left(-\frac{\hbar^2}{2m_i} \nabla^2 \right) + V(\vec{x}_1, \dots, \vec{x}_N).\end{aligned}$$

There is only one other fact about multiple particle systems, *the Pauli Exclusion Principle*, which puts additional constraints on the $\Psi(\vec{x}_1, \dots, \vec{x}_N)$ beyond those imposed by the Time Independent Schrödinger Equation (25). We will discuss this principle in a later note. All that we will need for now to demonstrate the virial theorem is the knowledge that Ψ satisfies condition (25).

2.4.2 Proof

With the variational principle and the multiple particle Schrödinger equation in hand, the mathematics of the proof of the virial theorem is straight forward. Our proof will be based on the observation from the variational principle that if we “dilute” one of the eigenstates taking $\Phi_\lambda(\vec{x}_1, \dots, \vec{x}_N) \equiv \psi_n(\lambda\vec{x}_1, \dots, \vec{x}_N)$ then $E(\lambda) \equiv \mathcal{R}[\Phi_\lambda] = (\Phi_\lambda, \hat{H}\Phi_\lambda)/(\Phi_\lambda, \Phi_\lambda)$ is stationary about the value $\lambda = 1$ ($\frac{dE(\lambda=1)}{d\lambda} = 0$) because here $\Phi_{\lambda=1}$ is just the *eigenstate* $\psi_n(\vec{x}_1, \dots, \vec{x}_N)$. To prove the virial theorem we now evaluate $E(\lambda)$ and set $E'(\lambda = 1) = 0$.

First, we evaluate the denominator of $\mathcal{R}[\Phi_\lambda]$,

$$\begin{aligned}(\Phi_\lambda, \Phi_\lambda) &= \int d^3x_1 \dots \int d^3x_N |\Phi_\lambda(\vec{x}_1, \dots, \vec{x}_N)|^2 \\ &= \int d^3x_1 \dots \int d^3x_N |\psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N)|^2 \\ &= \int \frac{d^3u_1}{\lambda^3} \dots \int \frac{d^3u_N}{\lambda^3} |\psi_n(\vec{u}_1, \dots, \vec{u}_N)|^2 \quad ; \vec{u}_i = \lambda\vec{x}_i \\ &= \lambda^{-3N} \int d^3u_1 \dots \int d^3u_N |\psi_n(\vec{u}_1, \dots, \vec{u}_N)|^2 \\ &= \lambda^{-3N} (\psi_n, \psi_n) \\ &= \lambda^{-3N}\end{aligned}\tag{26}$$

Next we break the numerator into potential and kinetic parts,

$$(\Phi_\lambda, \hat{H}\Phi_\lambda) = (\Phi_\lambda, \hat{T} + \hat{V}\Phi_\lambda) = (\Phi_\lambda, \hat{T}\Phi_\lambda) + (\Phi_\lambda, \hat{V}\Phi_\lambda).$$

The potential part gives,

$$\begin{aligned}(\Phi_\lambda, \Phi_\lambda) &= \int d^3x_1 \dots \int d^3x_N |\Phi_\lambda(\vec{x}_1, \dots, \vec{x}_N)|^2 V(\vec{x}_1, \dots, \vec{x}_N) \\ &= \int d^3x_1 \dots \int d^3x_N |\psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N)|^2 V(\vec{x}_1, \dots, \vec{x}_N) \\ &= \int d^3x_1 \dots \int d^3x_N |\psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N)|^2 (\lambda^{-v} \lambda^v) V(\vec{x}_1, \dots, \vec{x}_N) \\ &= \lambda^{-v} \int d^3x_1 \dots \int d^3x_N |\psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N)|^2 \lambda^v V(\vec{x}_1, \dots, \vec{x}_N) \\ &= \lambda^{-v} \int d^3x_1 \dots \int d^3x_N |\psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N)|^2 V(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N) \\ &= \lambda^{-v} \int \frac{d^3u_1}{\lambda^3} \dots \int \frac{d^3u_N}{\lambda^3} |\psi_n(\vec{u}_1, \dots, \vec{u}_N)|^2 V(\vec{u}_1, \dots, \vec{u}_N) \quad ; \vec{u}_i = \lambda\vec{x}_i \\ &= \lambda^{-v-3N} \int d^3u_1, \dots \int d^3u_N |\psi_n(\vec{u}_1, \dots, \vec{u}_N)|^2 V(\vec{u}_1, \dots, \vec{u}_N)\end{aligned}$$

$$\begin{aligned}
&= \lambda^{-v-3N} (\psi_n, \hat{V}\psi_n) \\
&= \lambda^{-v-3N} \langle V \rangle_n .
\end{aligned} \tag{27}$$

We now finish with the kinetic energy part which is a bit more difficult because of the differential form of the kinetic energy operator.

$$\begin{aligned}
(\Phi_\lambda, \hat{T}\Phi_\lambda) &= \int d^3x_1 \dots \int d^3x_N \psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N)^* \left[\sum_i \left(-\frac{\hbar^2}{2m_i} \right) \nabla_{\vec{x}_i}^2 \right] \psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N) \\
&= \int d^3x_1 \dots \int d^3x_N \psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N)^* \left[\sum_i \left(-\frac{\hbar^2}{2m_i} \right) \lambda^2 \nabla_{\lambda\vec{x}_i}^2 \right] \psi_n(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N) \\
&= \lambda^2 \int \frac{d^3u_1}{\lambda^3} \dots \int \frac{d^3u_N}{\lambda^3} \psi_n(\vec{u}_1, \dots, \vec{u}_N)^* \left[\sum_i \left(-\frac{\hbar^2}{2m_i} \right) \nabla_{\vec{u}_i}^2 \right] \psi_n(\vec{u}_1, \dots, \vec{u}_N) \quad ; \vec{u}_i = \lambda\vec{x}_i \\
&= \lambda^{2-3N} (\psi_n, \hat{T}\psi_n) \\
&= \lambda^{2-3N} \langle T \rangle_n .
\end{aligned} \tag{28}$$

Putting (26-28) together we have,

$$\begin{aligned}
E(\lambda) &= \frac{(\Phi_\lambda, \hat{H}\Phi_\lambda)}{(\Phi_\lambda, \Phi_\lambda)} = \frac{(\Phi_\lambda, \hat{T}\Phi_\lambda) + (\Phi_\lambda, \hat{V}\Phi_\lambda)}{(\Phi_\lambda, \Phi_\lambda)} = \frac{\lambda^{2-3N} \langle T \rangle_n + \lambda^{-v-3N} \langle V \rangle_n}{\lambda^{-3N}} \\
&= \lambda^2 \langle T \rangle_n + \lambda^{-v} \langle V \rangle_n .
\end{aligned}$$

As discussed above, this $E(\lambda)$ must be stationary about $\lambda = 1$,

$$\begin{aligned}
0 &= E'(\lambda = 1) \\
&= (2\lambda \langle T \rangle_n - v\lambda^{-v-1} \langle V \rangle_n) \Big|_{\lambda=1} \\
&= 2 \langle T \rangle_n - v \langle V \rangle_n .
\end{aligned}$$

From this follows directly the general virial theorem for systems with homogeneous potential interactions $V(\lambda\vec{x}_1, \dots, \lambda\vec{x}_N) = \lambda^v V(\vec{x}_1, \dots, \vec{x}_N)$,

$$\langle T \rangle_n = \frac{v}{2} \langle V \rangle_n . \tag{29}$$