

Lecture 5: Stationary States

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1 Definition of Stationary States

The main question we discuss here is *meaning of the energy conservation in Quantum Mechanics*. Our starting point in this case again should be the Classical Mechanics. In Classical Mechanics within Hamiltonian formulation the time dependence of any observable A_{cl} is defined by the relation:

$$\frac{dA_{cl}}{dt} = \frac{\partial A_{cl}}{\partial t} + \{A_{cl}, H_{cl}\} \quad (1)$$

where $\{\dots\}$ is a Poisson brackets.

The above equation applied to the classical Hamiltonian itself ($A_{cl} = H_{cl}$) means that it becomes energy independent observable if there is no explicit time dependence in H_{cl} . Such a function represents the conserved classical energy of the system.

Based on the correspondence principle - (I), one now assumes that there should be similar to H_{cl} observable also in Quantum Mechanics which is explicitly time independent. Since for any quantum mechanical observable one can associate an operator. Then naturally this will corresponds to the Hamiltonian operator which is explicitly time independent: \hat{H} .

Given such Hamiltonian operator one can now define the *Stationary States* as eigenstates of this Hamiltonian.

$$\hat{H} | \psi_n(t, q) \rangle = E_n | \psi_n(t, q) \rangle \quad (2)$$

with time independent eigenvalues E_n . Here q is the generic variable on which Hamiltonian operator, \hat{H} depends on. Note that the similar equation is true also for the continuous spectrum of the energy eigenstates E_n . Below we will use notations E and $| \psi_E(q, t) \rangle$ to identify the case with continuous eigenstates. According to the above definition the meaning of the energy conservation in Quantum Mechanics is that if at $t = t_0$ the eigenvalue of the Hamiltonian was E_n , then it is E_n for any other time.

1.1 Time dependence of the Stationary States

Using Schroedinger equation from Lecture 4 (Eq.(.)) one can obtain the time dependence of the stationary states as follows:

$$i\hbar \frac{d | \psi_n(t, q) \rangle}{dt} = \hat{H} | \psi_n(t, q) \rangle = E_n | \psi_n(t, q) \rangle \quad (3)$$

where in the RHS part of the equation we used the fact that $|\psi_n(t)\rangle$ is an eigenstate of \hat{H} . The above differential equation can be explicitly solved for the t dependence part of the state vector by the method of separable variables. Since E_n is t independent one can express the solution in the form:

$$|\psi_n(t, q)\rangle = A |\phi_n(t)\rangle |\psi_n(q)\rangle, \quad (4)$$

where A is a constant. Inserting the above state vector in Eq.(3) one obtains simple first order differential equation for the time dependent part of the stationary state vector:

$$i\hbar \frac{d}{dt} |\phi_n(t)\rangle = E_n |\phi_n(t)\rangle \quad (5)$$

which has a solution in the form:

$$|\phi_n(t)\rangle = B e^{-i\frac{E_n}{\hbar}t}, \quad (6)$$

where B is the constant of integration. Inserting above solution into Eq.(4) for the stationary state vector one obtains:

$$|\psi_n(t, q)\rangle = e^{-i\frac{E_n}{\hbar}t} |\psi_n(q)\rangle. \quad (7)$$

Here we absorbed the normalization constants into the state vector $|\psi(q)\rangle$.

Similarly for the continuous eigenvalue case one obtains:

$$|\psi_E(t, q)\rangle = e^{-i\frac{E}{\hbar}t} |\psi_E(q)\rangle. \quad (8)$$

Time Indeterminacy: It is worth comparing the solution of Eq.(7) to the solution of the free particle wave function with fixed momentum p_x :

$$\psi_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{i\frac{p_x}{\hbar}x} \quad (9)$$

This wave function as we discussed in the Lecture 4, is spread all over the space with constant probability density to be found anywhere. In this respect Eq.(7) can be considered analogous to Eq.(9) but in the time scale: that is the probability of observing energy E_n is constant at any given time interval.

Time Dependence of any given Quantum State: If we use Eq.(7) as an orthonormal basis, then we can express the time dependence of any given quantum state as superposition of stationary states in the form:

$$|\psi(t)\rangle = \sum_n a_n e^{-i\frac{E_n}{\hbar}t} |\psi_n(q)\rangle \quad (10)$$

where a_n are time independent coefficients.

1.2 Characterization of Eigenstates of Hamiltonian

Let us consider the several characteristics of eigenstates of Hamiltonian considering the discrete and continuous cases separately.

1.2.1 Spectrum

For the case of discrete spectrum the equation for the eigenstates and eigenvalues reads:

$$\hat{H} | \psi_n \rangle = E_n | \psi_n \rangle. \quad (11)$$

Since E_n represents a discrete real numbers one can define its minimal value calling it *ground state* or *K-state*. The full state the satisfies also Schroedinger equation according to Eq.(11) will be:

$$| \psi_n(t) \rangle = e^{-i\frac{E_n}{\hbar}t} | \psi_n \rangle \quad (12)$$

The above relations can be extended to the continuum range of energy spectrum. In this case the full wave function will read as:

$$| \psi_E(t) \rangle = e^{-i\frac{E}{\hbar}t} | \psi_E \rangle \quad (13)$$

with the normalization condition:

$$\langle \psi'_E(t) | \psi_E(t) \rangle = \delta(E' - E) \quad (14)$$

- *Wave Function*: One can define the wave function corresponding to the full quantum state (Eq.(13)) (for one-dimensional case):

$$\psi_n(x, t) = \langle \psi_x | \psi_n(t) \rangle \quad (15)$$

where $|\psi_x\rangle$ is the eigenstate of \hat{H} in Eq.(11). According our discussions in Lecture 4 the quantity $\rho_n(x) = |\psi_n(x, t)|^2$ will describe the coordinate distribution of the state. As it follows from Eq.(15) such a distribution is *time independent* - representing one of the main features of *stationary states*.

- *Expectation Values*: For the set of eigenstates the expectation value of any given observable A is:

$$\bar{A} = \sum_n \langle \psi_n(t) | \hat{A} | \psi_n(t) \rangle = \sum_n \langle \psi_n | \hat{A} | \psi_n \rangle, \quad (16)$$

where the RHS part of the equation is obtained based on the fact that we are working within Schroedinger picture in which the all operators of quantum mechanical observables are time independent and we also use the relation of Eq.(13). As one can see for stationary states the expectation values are *time independent* too.

- *Degenerate States*: If two eigenstates $|\psi_n\rangle$ and $|\psi_n'\rangle$ have same eigenvalue E_n , then such states are called *degenerate* states. It can be show that the degeneracy takes place once there are as minimum two hermitian operators \hat{f} and \hat{g} such that

$$[\hat{f}\hat{H}] = [\hat{g}\hat{H}] = 0 \quad \text{but} \quad [\hat{f}\hat{g}] \neq 0 \quad (17)$$

The degenerate states are characterized with several following properties:

- Any linear combination of degenerate states is an eigenstate of \hat{H} with the same eigenvalue
- Choice of an eigenstate for the degenerate states is not unique
- Degenerate states are not orthogonal, however it is possible to construct an orthogonal state with specific linear combination of the degenerate states

Example: One example of the degenerate stationary state is the free quantum state $|\psi_{E,p_x}\rangle$ which is an eigenstate of the \hat{p}_x and $\hat{H}_{free} = \frac{\hat{p}_x^2}{2m}$ operators:

$$\begin{aligned}\hat{p}_x |\psi_{E,p_x}\rangle &= p_x |\psi_{E,p_x}\rangle \\ \hat{H}_{free} |\psi_{E,p_x}\rangle &= \frac{p_x^2}{2m} |\psi_{E,p_x}\rangle.\end{aligned}\tag{18}$$

, Since the eigenvalue for the energy $E = \frac{p_x^2}{2m}$ it follows that two different eigenstates $|\psi_{E,p_x}\rangle$ and $|\psi_{E,-p_x}\rangle$ will have same eigenvalue for the energy. It will be interesting to identify what are those mutually noncommutative \hat{f} and \hat{g} operators that commute with \hat{H}_{free} .

- *Case of two (or more) Hamiltonians:* If $\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2)$ where q_1 and q_2 are independent parameters then, for the stationary state of \hat{H} , $|\psi_n\rangle$ one has

$$|\psi_n\rangle_n = |\psi_{n1}\rangle \times |\psi_{n2}\rangle \quad \text{with} \quad E_n = E_{n1} + E_{n2},\tag{19}$$

where $|\psi_{n1/n2}\rangle$ and $E_{n1/n2}$ are the eigenstates and eigenvalues of hamiltonian H_1 and H_2 respectively.

- *Space Localization of Bound and unbound States:* As we discussed above the stationary states can have discrete or continuous values of energy eigenvalues. This will correspond to the following condition for the normalization:

$$\begin{aligned}\langle \psi_n | \psi_n \rangle &= 1 && \text{for discrete states} \\ \langle \psi_{E'} | \psi_E \rangle &= \delta(E' - E) && \text{for continuous states}\end{aligned}\tag{20}$$

Introducing the wave functions for the above quantum states:

$$\psi_{n/E}(r) = \langle \psi_r | \psi_{n/E} \rangle\tag{21}$$

one can represent the Eq.(20) in the following form

$$\int |\psi_n(r)|^2 d^3r = 1 \quad \text{for discrete states}\tag{22}$$

and

$$\int \psi_{E'}^*(r) \psi_E(r) d^3r = \delta(E' - E) \quad \text{for continuous states}\tag{23}$$

where in both cases the integration is over the whole physical space.

The above two equations allow us to make conclusion about the space localization of the stationary states. For the discrete states since integrand is positive definitive, the integral over the infinite space can be finite only if the probability density is localized in the finite space decreasing at most exponentially at infinite distances from the main localization points. Such a situation will correspond to the system being **bound** - which will refer hereafter as **bound state**. For the case of the continues states. Eq.(23) indicates that in the limit of $E' \rightarrow E$ the integral diverges which will corresponds to the integrand being distributed over the infinite ranges in the space. Such a situation represents a probability density to be **unbound** - referring them as **unbound states**.

1.2.2 Schroedinger Equation for Stationary States

Since stationary states are eigenstates of hamiltonian operator, then using relation of Eq.(11) for the Schroedinger equation one obtains:

$$i\hbar \frac{d}{dt} | \psi_{n/E}(q, t) \rangle = \hat{H} | \psi_{n/E}(q, t) \rangle = E_{n/} | \psi_{n/E}(q, t) \rangle \quad (24)$$

Projecting the above equation to the coordinate space eigenstates for the Schroedinger wave equation one obtains:

$$i\hbar \frac{d}{dt} \psi_{n/E}(q, r, t) = -\frac{\hbar^2 \nabla^2}{2m} \psi_{n/E}(q, r, t) + V(r) \psi_{n/E}(q, r, t) = E_{n/} \psi_{n/E}(q, r, t) \quad (25)$$

1.3 Seven Pillars of Wisdom of Schroedinger Equation for Stationary States

Wisdom 1: *Properties of Stationary Wave Function.* For the stationary case we are dealing with the Schroedinger equation in the form:

$$-\frac{\hbar^2 \nabla^2}{2m} \psi_{n/E}(q, r, t) + V(r) \psi_{n/E}(q, r, t) = E_n \psi_{n/E}(q, r, t) \quad (26)$$

Supplemented with the probability density and density current as follows:

$$\begin{aligned} \rho(r) &= \psi_{n/E}^*(r) \psi_{n/E}(r) \\ \vec{j}(r) &= \frac{i\hbar}{2m} \left[\psi_{n/E}(r) \vec{\nabla} \psi_{n/E}^*(r) - \psi_{n/E}^*(r) \vec{\nabla} \psi_{n/E}(r) \right] = \frac{\hbar}{m} \text{Im} \psi_{n/E}^*(r) \vec{\nabla} \psi_{n/E}(r). \end{aligned} \quad (27)$$

The above equations we consider with the conditions that the probability density and the current are finite quantities having no singularities. These conditions imposes the following restrictions on the wave functions that should be a solution of Eq.(26).

- If the potential energy operator $V(r)$ is finite everywhere then $\psi_{n/E}$ should be finite and continuous everywhere.

- Additionally \vec{j} to be finite $\vec{\nabla}\psi_{n/E}(r)$ should be finite and finally to have finite solution for the eigenvalue of energy in Eq.(26) $\nabla\psi_{n/E}(r)$ also should be continuous such that $\nabla^2\psi_{n/E}(r)$ is finite too.

However in the case in which $V(r)$ has singularity the above conditions need to be amended with the condition that

- The $\hat{\nabla}\psi_{n/E}(r)$ should have discontinuity such that $\nabla^2\psi_{n/E}(r)$ will contain a singularity which will allow to cancel the singular part of $V(r)$ such that Eq.(26) will produce a finite results for E .

Wisdom 2: Energy Spectrum Inequality. If the potential energy has a minimum V_{min} then for any eigenstate of the Hamiltonian (including the ground state):

$$E_n \geq V_{min} \quad (28)$$

This statement can be proved noticing that for any given quantum state one can have relation:

$$\langle \psi | \hat{H} | \psi \rangle = \langle \psi | \hat{T} | \psi \rangle + \langle \psi | \hat{V} | \psi \rangle \geq \langle \psi | \hat{V} | \psi \rangle \geq V_{min}, \quad (29)$$

where in the above equation we used the fact that $\langle \psi | \hat{T} | \psi \rangle \geq 0$. Since this inequality is correct for any state vector $|\psi\rangle$, by choosing them to be the eigenstate of \hat{H} Hamiltonian, $|\psi_n\rangle$ with corresponding to the eigenvalue of E_n one obtains the relation of Eq.(28).

Wisdom 3: Bound and Unbound Quantum States. Let us consider a potential that disappears at infinite distances. For the one-dimensional example:

$$V(x) |_{|x| \rightarrow \infty} = 0 \quad (30)$$

The one can prove that the spectrum of **negative** energy states can be only **discrete** and represent a bound state, while **positive** energy spectrum corresponds to the continuous quantum states.

• We start with considering the negative energy case $E < 0$. Considering now the Eq.(26) in the $|x| \rightarrow \infty$ limit where the potential energy is negligible one obtains:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = -|E| \psi(x), \quad (31)$$

which has a finite solutions in the form of:

$$\psi(x) = C e^{-\kappa|x|} \quad (32)$$

where $\kappa = \frac{\sqrt{2m|E|}}{\hbar}$. In the above wave function the constant C can be fixed to achieve a normalization condition:

$$\int_{-\infty}^{\infty} |\psi(x)|^2 dx = 1, \quad (33)$$

which according to our discussion in Eq.(20) corresponds to the **discrete** spectrum of the **bound state**.

• Considering now the positive energy spectrum $E > 0$ for Eq.(26) at large distances $|x| \rightarrow \infty$ one obtains:

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E \psi(x), \quad (34)$$

which has a solutions in the form of:

$$\psi(x) = Ae^{-ikx} + Be^{ikx}, \quad (35)$$

where $k = \frac{\sqrt{2mE}}{\hbar}$. With appropriate arrangements of constants A and B the above solution can be normalized as:

$$\int_{-\infty}^{\infty} \psi_{k'}(x) \psi_k(x) dx = \delta(k' - k). \quad (36)$$

According to our discussion in Eq.(20) such a normalization will corresponds to the wave function representing an **unbound** wave function with **continuous** values for energy.

Thus the above discussion introduces a concept of absolute negative energy of the system. That is if potential energy disappears at infinity then the constituents of bound system should necessarily have a negative values of energy.

Wisdom 4: Quantum Tunneling. The one profound conclusion from the previous discussion is that one can not trap the positive energy particle by the potential barrier that disappears at infinity. This is the foundation of the **Quantum Tunneling** effect according to which the positive energy particle trapped by the potential barrier will tunnel out from the trap and has finite probability to appear at distances outside to the potential energy region. Such a tunneling also indicates a possibility of the quantum particles to be in the state in which its energy $E < V(x)$.

Wisdom 5: Stability of a bound system: Let us consider a potential energy that behaves as:

$$V(r) = -\frac{\alpha}{r^s}, \quad (37)$$

and consider a quantum state confined to the region of $r \leq r_0$. In this case since the uncertainty of position is in the order of r_0 and one expects that for a stationary system the average momentum is close to zero the rms value of the momentum according to the uncertainty principle

$$p_{rms}^2 \sim \frac{\hbar^2}{r_0^2} \quad (38)$$

Using this relation one can estimate the expectation value of the kinetic energy for a given stationary state to be:

$$\langle T \rangle \sim \frac{\hbar^2}{2mr_0^2} \quad (39)$$

and expectation value of the energy of the quantum system:

$$\bar{E} \approx \langle T \rangle + \langle V \rangle = \frac{\hbar^2}{2mr_0^2} - \frac{\alpha}{r_0^s} \quad (40)$$

From above relation one observes that if $s > 2$, \bar{E} can be arbitrarily negative at small r_0 . Moreover there are bound states with $\bar{E} \rightarrow -\infty$ localized at $r_0 \rightarrow 0$. Such a situation allows the ground state (with infinitely large binding energy) to be at the position r_0 which corresponds to the quantum system falling (or imploding) into the center.

If however, $s < 2$ then \bar{E} can not be arbitrarily negative. If initially $\bar{E} < 0$ then approaching towards the center there is always some r_0^{min} at which $\bar{E} \geq 0$. Thus the bound system can not fall into the center and will have minimal dimensions of order of $\sim r_0^{min}$. This result indicates that the bound quantum system with $s < 2$ will have stability at finite distances and therefore will be able to sustain a structure.

Since Coulomb interaction behaves as $-\frac{\alpha}{r}$, that is $s = 1$, the above results explains why atoms are stable and electrons are not falling to the center as it follows from Classical Electrodynamics.

Wisdom 6: *Characteristics of the energetic spectrum in dependence of the behavior of potential energy V at infinity.*

Let's consider again $V|_{r \rightarrow \infty} \rightarrow 0$ and being negative as in Eq.(37). Consider now the wave packet concentrated at $r_0 \rightarrow r_0 + \Delta r$ such that $\Delta r \sim \epsilon r_0$, then one can estimate the expectation values of kinetic energy as:

$$\langle T \rangle \sim \frac{\hbar^2}{2m\Delta^2 r_0} = \frac{\hbar^2}{2m\epsilon^2 r_0^2} \quad (41)$$

resulting in:

$$\bar{E} \approx \langle T \rangle + \langle V \rangle = \frac{\hbar^2}{2m\epsilon^2 r_0^2} - \frac{\alpha}{r_0^s}. \quad (42)$$

From above equation one observes that if $s < 2$ then at some large r_0 one will have $\bar{E} \leq 0$ resulting in a stationary bound states with ver large r_0 . The interesting property of these bound states is that at $r_0 \rightarrow \infty$ corresponds to :

$$\bar{E} \approx \sim -\frac{\alpha}{r_0} \rightarrow 0 \quad (43)$$

which represents bound energy spectrum with its magnitude and relative spacing approaching to 0. Thus the discrete energy spectrum that corresponds to $E_n \rightarrow 0$ with infinite number of the states will indicate on the working of the potential of Eq.(37) with $s < 2$. One such example is the **Coulomb** interaction.

If however $s > 2$ \bar{E} becomes positive at some small r_0 and number of negative states are finite with finite spacing between relative energy states.

Wisdom 7: *The Time reversal in quantum mechanics.* One of the outstanding properties of *Classical Mechanics* is that for closed systems the invariance of the physical laws with respect

to the time reversal $t \rightarrow -t$. It is interesting to see whether such an invariance is preserved in Quantum Mechanics. The answer is not trivial since in this fundamental level the reality is described by the *state vector* rather than say coordinates r_i and momenta p_i like in Hamiltonian formulation of Classical Mechanics. Since quantum mechanical analogue of classical closed systems is the condition for the stationary states, to check the time reversal property one needs to consider Schroedinger equation for the stationary states:

$$i\hbar \frac{d}{dt} | \psi(q, t) \rangle = \left(\frac{p^2}{2m} + V \right) | \psi(q, t) \rangle = E | \psi(q, t) \rangle. \quad (44)$$

Applying time reversal transformation to the above equation one obtains:

$$-i\hbar \frac{d}{dt} | \psi(q, t) \rangle = \left(\frac{p^2}{2m} + V \right) | \psi(q, t) \rangle = E | \psi(q, t) \rangle. \quad (45)$$

Comparing above two equations one observes that Eqs.(46) coincides with Eq.(46) only if one considers the complex conjugate of it, i.e.

$$i\hbar \frac{d}{dt} | \psi^*(q, t) \rangle = \left(\frac{p^2}{2m} + V \right) | \psi^*(q, t) \rangle = E | \psi^*(q, t) \rangle. \quad (46)$$

thus we conclude that the time reversal invariance in quantum mechanics need to be generalized to the requirement of the invariance with respect to the wider transformation, such as:

$$t \rightarrow -t \quad \text{and} \quad | \psi \rangle \rightarrow | \psi^* r \rangle \quad (47)$$

2 Virial Theorem

As we observed above the stationary states have the most simple time dependence defined by their energy eigenvalues. This fact results in the new relationship between operators of kinetic and potential energies - commonly referred as *Virial Theorem*

To start we recall the energy dependence of the expectation value any given operator \hat{Q} :

$$\frac{d\langle \hat{Q} \rangle}{dt} = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle + \frac{\partial \langle \hat{Q} \rangle}{dt}. \quad (48)$$

Since the time dependence of the stationary states are defined as in Eq.(7) and we are working within the Schroedinger representation of Quantum Mechanics in which operators are time independent, from the above equation one obtains that the time dependence of the expectation values of operators is defined solely by the comutator of a given operator and Hamiltonian, i.e.

$$\frac{d\langle \hat{Q} \rangle}{dt} = \frac{i}{\hbar} \langle [\hat{H}, \hat{Q}] \rangle. \quad (49)$$

If now further we choose operator \hat{Q} such that it is diagonal in time, i.e. does not alter the time dependence of the stationary state for which expectation value is calculated then one obtains $\frac{d\langle\hat{Q}\rangle}{dt} = 0$ resulting in

$$\langle[\hat{H}, \hat{Q}]\rangle = 0. \quad (50)$$

This relation in principle we can call *generalized Virial Theorem*. For particular example we now consider the case: $\hat{Q} = \hat{x}\hat{p}$ obtaining:

$$\langle[\hat{H}, \hat{x}\hat{p}]\rangle = \langle[\hat{H}, \hat{x}]p\rangle + \langle\hat{x}[\hat{H}, \hat{p}]\rangle = 0, \quad (51)$$

where in the above expression we used the relation:

$$[A, BC] = [AB]C + B[AC]. \quad (52)$$

We now consider the commutators in Eq.(51) separately. Using the generic form of the Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V}(x)$ as well as commutation relation $[\hat{x}\hat{p}] = i\hbar$

$$[\hat{H}, \hat{x}] = \left[\frac{\hat{p}^2}{2m} + \hat{V}(x), \hat{x}\right] = \left[\frac{\hat{p}^2}{2m}, \hat{x}\right] = \frac{1}{2m}[\hat{p}^2, \hat{x}] = -\frac{1}{2m}([\hat{x}\hat{p}]\hat{p} + \hat{p}[\hat{x}\hat{p}]) = -\frac{1}{2m}(2i\hbar\hat{p}) = -\frac{i\hbar p}{m}. \quad (53)$$

Next, using the commutator relation $[\hat{F}(x), \hat{p}] = i\hbar\frac{dF(x)}{dx}$ for any continuous function of $F(\hat{x})$ one obtains

$$[\hat{H}, \hat{p}] = [\hat{V}, \hat{p}] = i\hbar\frac{d\hat{V}(x)}{dx}. \quad (54)$$

Note that in this case $\hat{V}(x)$ is understood as V being continuous function of operator \hat{x} . Inserting Eqs.(53) and (54) into Eq.(51) one obtains

$$\langle -i\hbar\frac{\hat{p}^2}{m} \rangle + \langle i\hbar\hat{x}\frac{d\hat{V}(x)}{dx} \rangle = 0, \quad (55)$$

which can be rearranged in the form of

$$2\langle\hat{T}\rangle = \langle\hat{x}\frac{d\hat{V}(x)}{dx}\rangle. \quad (56)$$

The above relation represents the Virial Theorem for one-dimensional case.

Considering the same derivation for each $i = 1, 2, 3$ components separately, the above expression can be generalized for the three-dimensional case as follows:

$$2\langle\hat{T}\rangle = \langle\hat{\vec{r}} \cdot \vec{\nabla}\hat{V}(r)\rangle. \quad (57)$$

3 Examples of Application of Virial Theorem

3.1 Harmonic Oscillator

For one-dimensional Harmonic oscillator one can use the virial theorem to calculate its RMS distance. For this we note that expectation value of the Hamiltonian based on its eigenstates is:

$$\langle H \rangle = (n + \frac{1}{2})\hbar\omega = \langle T \rangle + \langle V \rangle \quad (58)$$

where $V(x) = \frac{1}{2}m\omega^2x^2$. Using the Virial theorem one obtains:

$$2\langle T \rangle = \langle x \frac{dV}{dx} \rangle = 2\langle V \rangle = m\omega^2\langle x^2 \rangle \quad (59)$$

From the above relation it follows that $\langle T \rangle = \langle V \rangle$ therefore from Eq.(58) one obtains:

$$2\langle V \rangle = (n + \frac{1}{2})\hbar\omega \quad (60)$$

Using now the relation $\langle V \rangle = \frac{1}{2}m\omega^2\langle x^2 \rangle$ one obtains:

$$\langle x^2 \rangle = \frac{(n + \frac{1}{2})\hbar}{m\omega}. \quad (61)$$

This result indicates that the square of the RMS radii of one-dimensional oscillator increases linearly with the excitation energy.

3.2 Single Electron Atom

One can use the Virial Theorem to estimate the radius of a single electron atom as a function of its excitation energy. We consider an electron in the Coulomb field of Z proton nucleus:

$$V(r) = -\frac{Z\alpha\hbar c}{r} \quad (62)$$

where $\alpha = \frac{e^2}{\hbar c} = 1/137.036$. The energy levels of the electron in such atom are:

$$E_n = -\frac{Z^2\alpha^2mc^2}{2n^2}. \quad (63)$$

Using now the Virial Theorem for three-dimensional case one obtains:

$$2\langle \hat{T} \rangle \langle \hat{r} \cdot \vec{\nabla} \hat{V}(r) \rangle = -Z\alpha\hbar c \langle r \frac{d}{dr} (\frac{1}{r}) \rangle = Z\alpha\hbar \langle \frac{1}{r} \rangle = -\langle V(r) \rangle. \quad (64)$$

Using this relation and the expectation value for the Hamiltonian using its eigenstates one obtains:

$$\langle H \rangle = \langle T \rangle + \langle V \rangle = \frac{1}{2}\langle V \rangle. \quad (65)$$

Now using the fact that $\langle H \rangle = E_n$ and Eq.(62) from the above equation we can estimate the average radius of the atom

$$\left\langle \frac{1}{r} \right\rangle = 2 \frac{1}{Z\alpha\hbar c} \frac{Z^2\alpha^2 mc^2}{2n^2} = \frac{Z\alpha mc}{\hbar n^2}. \quad (66)$$

The interesting result here is that while for Harmonic Oscillator the size of the system grows like $\sim \sqrt{n}$, for single electron atom it grows as $\sim n^2$.