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Perturbation Theory

Exact solutions are available for very few problems in quantum world. For almost all real problems are to be solved by approximation methods. Perturbation theory is one of them.

This theory is applied in cases where we want to measure the response of atoms and molecules to external (electric or magnetic) field: Effect of small change in potential on quantum system.

Example : interaction between two electrons in He atom

Perturbation mean small disturbance. When some external factors affect the system and the exact solution is not available, then the external factor affecting the system, is considered as a small perturbation to the system to find out the solution to explain its behavior and energy.

- This theory can be applied to both Time Independent and Time Dependent system. Approach of perturbation treatment towards degenerate and non degenerate system is also different. We shall restrict our application to **time independent non degenerate perturbation theory**. This approach is known as Rayleigh-Schrödinger Perturbation Theory.

- Time Independent Perturbation Theory

  The Hamiltonian of a quantum mechanical system with small perturbation may be represented as H whose exact solution is difficult to find

$$\hat{H}\psi_n = E_n\psi_n \qquad (1)$$

$H^{(0)}$ is the Hamiltonian for the unperturbed or simpler system, its exact solution is known.

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \qquad (2)$$

$\Psi_n^{(0)}$ s are the exact solution for unperturbed system and non-degenerate

The difference between H and $H^{(0)}$ is very small and may be considered as perturbation on $H^{(0)}$ and it is very small, all quantities of the system can be expanded in terms of Taylor Series stating from unperturbed quantities. Hence:

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}^{(1)} + \lambda^2 \hat{H}^{(2)} + \cdots \quad (3)$$

$$\psi_n = \psi_n^{(0)} + \lambda \psi_n^{(1)} + \lambda^2 \psi_n^{(2)} + \cdots \quad (4)$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \quad (5)$$

Here the parameter $\lambda \rightarrow 0$

- **For information: Taylor series and its examples**:

$$\begin{aligned} f(x) &= f(x_0) + f'(x_0)(x - x_0) + \frac{f''(x_0)}{2!}(x - x_0)^2 \\ &\quad + \frac{f'''(x_0)}{3!}(x - x_0)^3 + \frac{f''''(x_0)}{4!}(x - x_0)^4 + \cdots \\ &= \sum_{n=0}^{\infty} \frac{f^{(n)}(x_0)}{n!}(x - x_0)^n. \end{aligned}$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \ldots$$

$$\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \frac{x^7}{7!} + \ldots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \frac{x^6}{6!} + \ldots$$

$$\ln(1 + x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \ldots \quad for\,|x| < 1$$

$$\tan^{-1}(x) = x - \frac{x^3}{3} + \frac{x^5}{5} - \frac{x^7}{7} + \ldots \quad for\,|x| < 1$$

- Following Taylor expansion we may write $E_n(\lambda)$ around $\lambda \rightarrow 0$ as

$$E_n = E_n(0) + \left.\frac{dE_n}{d\lambda}\right|_{\lambda=0} \lambda + \frac{1}{2!}\left.\frac{d^2E_n}{d\lambda^2}\right|_{\lambda=0} \lambda^2 + \frac{1}{3!}\left.\frac{d^3E_n}{d\lambda^3}\right|_{\lambda=0} \lambda^3 + \cdots \qquad (6)$$

comparing eq (5) with eq (6), one may write:

$$E_n^{(0)} = E_n(0), \quad E_n^{(1)} = \frac{dE_n}{d\lambda}\Big|\lambda=0,$$

$$E_n^{(2)} = \frac{1}{2!}\frac{d^2E_n}{d\lambda^2}\Big|\lambda=0$$

etc. Similar relation holds for Hamiltonian and wavefunction

In many physical situation, it is sufficient to consider upto 1st order term, hence the series is terminated up to $H=H^{(0)} + H^{(1)}$

Now to calculate the perturbation correction, we substitute eq (3), (4) and (5) in eq (1) and rearrange the terms according to the powers of λ

$$\begin{aligned} & \{\hat{H}^{(0)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(0)}\} \\ + \; & \lambda\{\hat{H}^{(0)}\psi_n^{(1)} + \hat{H}^{(1)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(1)} - E_n^{(1)}\psi_n^{(0)}\} \\ + \; & \lambda^2\{\hat{H}^{(0)}\psi_n^{(2)} + \hat{H}^{(1)}\psi_n^{(1)} + \hat{H}^{(2)}\psi_n^{(0)} - E_n^{(0)}\psi_n^{(2)} - E_n^{(1)}\psi_n^{(1)} - E_n^{(2)}\psi_n^{(0)}\} \\ + \; & \cdots = 0 \end{aligned} \tag{7}$$

The powers of λ are linearly independent functions, so to satisfy the above equation for all arbitrary values of λ, only criteria I to equate the coefficient of each power to be 0.

$$\hat{H}^{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \quad (8)$$

$$(\hat{H}^{(0)} - E_n^{(0)})\psi_n^{(1)} = (E_n^{(1)} - \hat{H}^{(1)})\psi_n^{(0)} \quad (9)$$

$$(\hat{H}^{(0)} - E_n^{(0)})\psi_n^{(2)} = (E_n^{(2)} - \hat{H}^{(2)})\psi_n^{(0)} + (E_n^{(1)} - \hat{H}^{(1)})\psi_n^{(1)} \quad (10)$$

$$\cdots$$

Now onwards, we shall be using Bra-Ket notations to simplify the equation, here wave function corrections by there state number will be written as $\Psi_n^{(0)} = |n^{(0)}\rangle$, $\Psi_n^{(1)} = |n^{(1)}\rangle$

The first order Correction to Energy

We shall start from eq (9)

$$(\hat{H}^{(0)} - E_n^{(0)})|n^{(1)}\rangle = (E_n^{(1)} - \hat{H}^{(1)})|n^{(0)}\rangle \quad (11)$$

Multiplying eq (11) from left by $< n^{(0)}|$, we obtain

$$\langle n^{(0)}|(\hat{H}^{(0)} - E_n^{(0)})|n^{(1)}\rangle = \langle n^{(0)}|(E_n^{(1)} - \hat{H}^{(1)})|n^{(0)}\rangle \quad (12)$$

$$\langle n^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle - E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle = E_n^{(1)}\langle n^{(0)}|n^{(0)}\rangle - \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \quad (13)$$

$$E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle - E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle = E_n^{(1)} - \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \quad (14)$$

$$0 = E_n^{(1)} - \langle n^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \quad (15)$$

In order to go from eq (13) to (14) we have used the fact that unperturbed wavefunction is normalised and the Hermiticity of $H^{(0)}$, as a result we can write it as

$$\langle n^{(0)}|\hat{H}^{(0)}|n^{(1)}\rangle = \langle(\hat{H}^{(0)}n^{(0)})|n^{(1)}\rangle = \langle(E_n^{(0)}n^{(0)})|n^{(1)}\rangle = E_n^{(0)}\langle n^{(0)}|n^{(1)}\rangle \quad (16)$$

Hence according to (15), we can write the first order of energy as

$$E_n^{(1)} = \langle n^{(0)} | \hat{H}^{(1)} | n^{(0)} \rangle \qquad (17)$$

It is Simply the **expectation value of 1st order Hamiltonian in the unperturbed state**

Solve the problem: Calculate the first order correction to the energy of th nth state of a harmonic oscillator hoe centre of potential had been diplacd from 0 to ditance a

First oder correction of wave function:

At first eq (9) is multiplied from left by $< k^{(0)} |$, where k $\neq$ n,

$$\langle k^{(0)}|\hat{H}^{(0)} - E_n^{(0)}|n^{(1)}\rangle = \langle k^{(0)}|E_n^{(1)} - \hat{H}^{(1)}|n^{(0)}\rangle \quad (23)$$

$$(E_k^{(0)} - E_n^{(0)})\langle k^{(0)}|n^{(1)}\rangle = -\langle k^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle \quad (24)$$

$$\langle k^{(0)}|n^{(1)}\rangle = \frac{\langle k^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} \quad (25)$$

Where we have made use of the orthogonally of the zeroth order wave functions and also have assumed non-degeneracy of zeroth order problem (i.e. $E_n^{(0)} - E_k^{(0)} \neq 0$)

Now to derive the expression for $|n^{(1)}\rangle$ we will employ the idea of identity operator in the eigen functions of unperturbed system (zeroth order eigen functions)

$$|n^{(1)}\rangle = \hat{1}|n^{(1)}\rangle = \sum_k |k^{(0)}\rangle\langle k^{(0)}|n^{(1)}\rangle \tag{26}$$

Before substituting (25) into the above equation we must resolve a conflict: k must be different from n in (25) but not necessarily so in (26). This restriction implies that the first order correction to $|n\rangle$ will contain no contribution from $|n^{(0)}\rangle$. To impose this restriction we require that that $\langle n^{(0)}|n\rangle = 1$ (this leads to $\langle n^{(0)}|n^{(j)}\rangle = 0$ for $j \geq 1$. Prove it!) instead of $\langle n|n\rangle = 1$. This choice of normalisation for $|n\rangle$ is called *intermediate normalisation* and of course it does not affect any physical property calculated with $|n\rangle$ since observables are independent of the normalisation of wavefunctions. So now we can substitute (25) into (26) and get

$$|n^{(1)}\rangle = \sum_{k\neq n} |k^{(0)}\rangle \frac{\langle k^{(0)}|\hat{H}^{(1)}|n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}} = \sum_{k\neq n} |k^{(0)}\rangle \frac{H_{kn}^{(1)}}{E_n^{(0)} - E_k^{(0)}} \tag{27}$$

where the matrix element $H_{kn}^{(1)}$ is defined by the above equation.

- Second Order Energy Correction

To derive an expression for the second order correction to the energy multiply (10) from the left with $\langle n^{(0)}|$ to obtain

$$\begin{aligned} \langle n^{(0)}|\hat{H}^{(0)} - E_n^{(0)}|n^{(2)}\rangle &= \langle n^{(0)}|E_n^{(2)} - \hat{H}^{(2)}|n^{(0)}\rangle + \langle n^{(0)}|E_n^{(1)} - \hat{H}^{(1)}|n^{(1)}\rangle \\ 0 &= E_n^{(2)} - \langle n^{(0)}|\hat{H}^{(2)}|n^{(0)}\rangle - \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle \end{aligned} \tag{28}$$

where we have used the fact that $\langle n^{(0)}|n^{(1)}\rangle = 0$ (section 2.1.2). We now solve (28) for $E_n^{(2)}$

$$E_n^{(2)} = \langle n^{(0)}|\hat{H}^{(2)}|n^{(0)}\rangle + \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle = H_{nn}^{(2)} + \langle n^{(0)}|\hat{H}^{(1)}|n^{(1)}\rangle \tag{29}$$

which upon substitution of $|n^{(1)}\rangle$ by the expression (27) becomes

$$E_n^{(2)} = H_{nn}^{(2)} + \sum_{k\neq n} \frac{H_{nk}^{(1)} H_{kn}^{(1)}}{E_n^{(0)} - E_k^{(0)}} \ . \tag{30}$$

Variational Theory

Variation theory is another common approximation method in quantum mechanics.

Perturbation theory I useful when there is a small dimensionless parameter (λ) in the problem and the system is exactly solvable when $\lambda \rightarrow 0$. (He atom problem, quantum electrodynamics)

In case of variational theoy, above criteria are not required. Therefore it is useful to study in studying strongly correlated systems. This theory is the basis of Hatree-Fock theory, density function theory This Theory is useful to study the ground state.

This theorem is based on Ritz Theorem, which states that, given a time independent Hamiltonian, H, with a set of eigenvalues, E_n and eigenvectors, $|\psi_n\rangle$ satisfying

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

then for any arbitrary ket vector $|\psi\rangle$ in the Hilbert space, the expectation value of H in this ket must satisfy

$$\langle H\rangle \equiv \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

where E_0 is the exact ground state energy. Equality only holds if

$$|\psi\rangle = |\psi_0\rangle$$

The proof of the theorem is relatively simple. We expand $|\psi\rangle$ in the eigenstates of H:

$$|\psi\rangle = \sum_n C_n|\psi_n\rangle$$

Then

$$\langle\psi|\psi\rangle = \sum_{m,n} C_n^* C_m \langle\psi_n|\psi_m\rangle = \sum_n |C_n|^2$$

and

$$\langle\psi|H|\psi\rangle = \sum_{m,n} C_n^* C_m \langle\psi_n|H|\psi_m\rangle = \sum_{m,n} C_n^* C_m E_n \delta_{mn} = \sum_n E_n|C_n|^2$$

Therefore, the expectation value of H in the arbitrary ket vector is

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} = \frac{\sum_n E_n|C_n|^2}{\sum_n |C_n|^2}$$

Since $|C_n|^2 \geq 0$ and $E_n \geq E_0$, it follows that

$$\frac{\sum_n E_n|C_n|^2}{\sum_n |C_n|^2} \geq \frac{E_0 \sum_n |C_n|^2}{\sum_n |C_n|^2} = E_0$$

Therefore, we have

$$\frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} \geq E_0$$

It is also clear that equality can only hold if $C_0 = 1$ and $C_n = 0$, $n > 0$, in which case,

$$|\psi\rangle = |\psi_0\rangle$$

The conclusion is that E_0 is, therefore, a lower bound on the on $\langle H\rangle$, which means that we can approximate E_0 by a minimization of $\langle H\rangle$ with respect to any parameters that $|\psi\rangle$ might depend on.

Note that

$$\langle H \rangle = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

depends on *all* components of $|\psi\rangle$. If we write the expectation values as integrals (in one-dimension, for example), then we see that

$$\langle H \rangle = \frac{\int \, dx \; \psi^*(x) H \psi(x)}{\int \, dx \; \psi^*(x) \psi(x)}$$

which shows that $\langle H \rangle$ depends on all values of the function $\psi(x)$, which is known as a *trial wave function.* We, therefore, call $\langle H \rangle$ a *functional* of $\psi(x)$. Loosely speaking, a functional is a function of a function. We, therefore, denote the variational functional as

$$E[\psi] = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

from which it follows that

$$E[\psi] \geq E_0$$
$$E[\psi_0] = E_0$$

The functional character of $E[\psi]$ can be used to derive another important property of the functional, which is the stationarity property around any eigenstate of H. In order to derive the stationarity condition, we consider making a small variation of the trial ket according to

$$|\psi\rangle \longrightarrow |\psi\rangle + |\delta\psi\rangle$$
$$\langle\psi| \longrightarrow \langle\psi| + \langle\delta\psi|$$

and we evaluate the functional $E[\psi + \delta\psi]$:

$$E[\psi + \delta\psi] = \frac{[\langle\psi| + \langle\delta\psi|]\, H\, [|\psi\rangle + |\delta\psi\rangle]}{[\langle\psi| + \langle\delta\psi|]\, [|\psi\rangle + |\delta\psi\rangle]}$$

Now, we work to first order in $|\delta\psi\rangle$ or $\langle\delta\psi|$. Thus, we expand the functional:

$$E[\psi + \delta\psi] = E[\psi] + \frac{\partial E}{\partial\langle\psi|}\langle\delta\psi| + \frac{\partial E}{\partial|\psi\rangle}|\delta\psi\rangle + \cdots$$

and the right side becomes

$$\begin{aligned}
\frac{\langle\psi|H\psi\rangle + \langle\delta\psi|H|\psi\rangle + \langle\psi|H|\delta\psi\rangle + \cdots}{\langle\psi|\psi\rangle + \langle\psi|\delta\psi\rangle + \langle\delta\psi|\psi\rangle + \cdots} &= \frac{\langle\psi|H\psi\rangle + \langle\delta\psi|H|\psi\rangle + \langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle}\left[1 - \frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle}\right] \\
&= \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\delta\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|H|\psi\rangle}{\langle\psi|\psi\rangle}\frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} \\
&= E[\psi] + \frac{\langle\delta\psi|H|\psi\rangle}{\langle\psi|\psi\rangle} + \frac{\langle\psi|H|\delta\psi\rangle}{\langle\psi|\psi\rangle} - E[\psi]\frac{\langle\psi|\delta\psi\rangle}{\langle\psi|\psi\rangle} - E[\psi]\frac{\langle\delta\psi|\psi\rangle}{\langle\psi|\psi\rangle} \\
&= E[\psi] + \langle\delta\psi|\left[\frac{H|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{E[\psi]|\psi\rangle}{\langle\psi|\psi\rangle}\right] + \left[\frac{\langle\psi|H}{\langle\psi|\psi\rangle} - \frac{\langle\psi|E[\psi]}{\langle\psi|\psi\rangle}\right]|\delta\psi\rangle
\end{aligned}$$

Now, comparing the left and right sides, we have

$$\begin{aligned}
\frac{\partial E}{\partial\langle\psi|} &= \frac{H|\psi\rangle}{\langle\psi|\psi\rangle} - \frac{E[\psi]|\psi\rangle}{\langle\psi|\psi\rangle} \\
\frac{\partial E}{\partial|\psi\rangle} &= \frac{\langle\psi|H\rangle}{\langle\psi|\psi\rangle} - \frac{\langle\psi|E[\psi]}{\langle\psi|\psi\rangle}
\end{aligned}$$

The stationarity condition is now obtained by setting the two first derivatives of $E[\psi]$ to zero, which yields to conditions:

$$H|\psi\rangle = E[\psi]|\psi\rangle$$
$$\langle\psi|H = \langle\psi|E[\psi]$$

which are equivalent, being simply adjoints of each other.

Thus, the stationary condition is

$$H|\psi\rangle = E[\psi]|\psi\rangle$$

which can be satisfied only if $|\psi\rangle$ is an eigenvector of H with eigenvalue $E[\psi]$. This suggests that any eigenvector of H can be found by searching the functional $E[\psi]$ for extrema. Although possible, in principle, this is very difficult to implement in practice unless the dimensionality of the system is very low. However, if anyone were able to come up with an efficient algorithm for doing so, the variational theory guarantees that the process will yield the eigenvectors of H.

Example-I: Harmonic Oscillator

We will use the harmonic oscillator Hamiltonian in order to illustrate the procedure of using the variational theory. The Hamiltonian we wish to consider, therefore, is

$$H = -\frac{h^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2$$

Suppose that we do not know the exact ground state solution of this problem, but, using intuition and knowledge of the shape of the potential, we postulate the shape of the wavefunction:

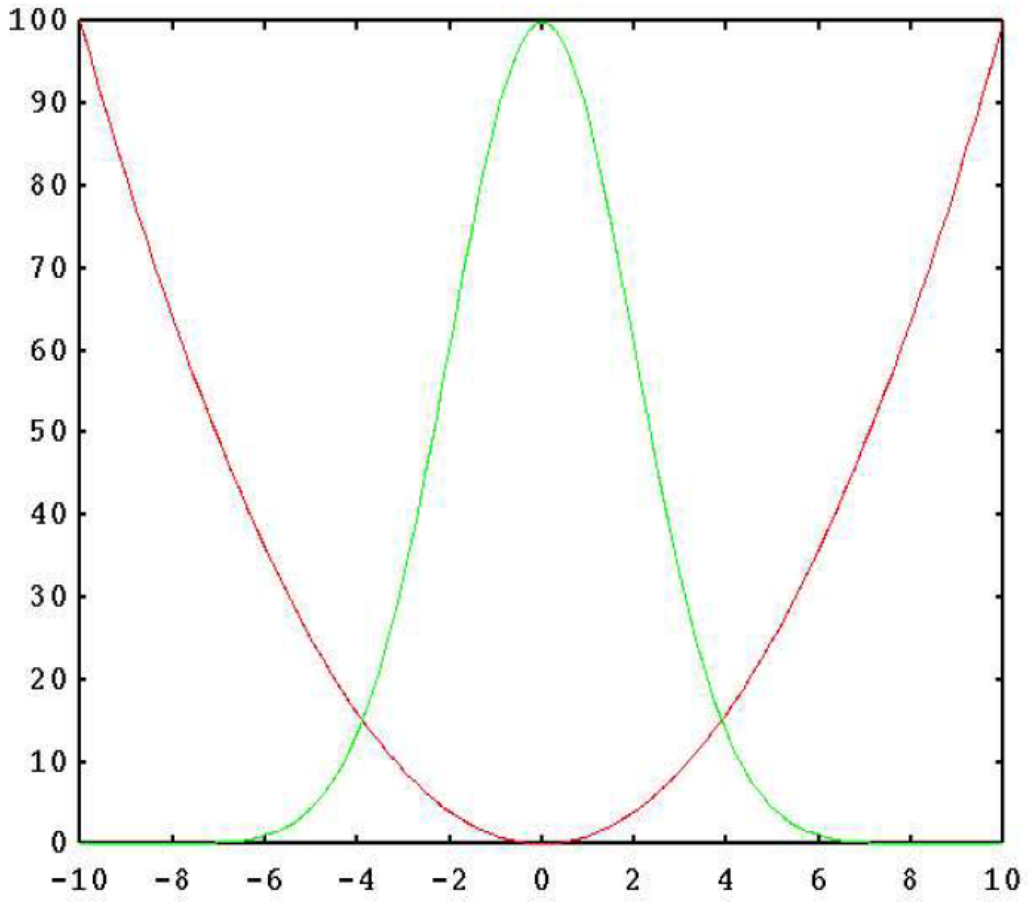

FIG. 1.

and postulate a form for the ground state wave function as

$$\psi(x) = e^{-\alpha x^2} \equiv \psi(x;\alpha)$$

We view α as a variational parameter with respect to which we can minimize $\langle H \rangle$.

Thus, we compute

$$E(\alpha) = \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle}$$

Clearly,

$$\langle \psi | \psi \rangle = \int_{-\infty}^{\infty} dx \; e^{-2\alpha x^2} = \sqrt{\frac{\pi}{2\alpha}}$$

The quantity

$$\langle \psi | H | \psi \rangle = \int_{-\infty}^{\infty} dx \; e^{-\alpha x^2} \left[-\frac{h^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m\omega^2 x^2 \right] e^{-\alpha x^2}$$

can be easily shown to be

$$\langle \psi | H | \psi \rangle = \left(\frac{\alpha h^2}{2m} + \frac{m\omega^2}{8\alpha} \right) \sqrt{\frac{\pi}{2\alpha}}$$

There, the ratio of these gives

$$E(\alpha) = \left(\frac{\alpha h^2}{2m} + \frac{m\omega^2}{8\alpha} \right)$$

We then compute the best approximation to E_0 by minimizing $E(\alpha)$ with respect to α:

$$E'(\alpha) = \frac{dE}{d\alpha} = 0$$

$$\frac{h^2}{2m} - \frac{m\omega^2}{8\alpha^2} = 0$$

$$\alpha^2 = \frac{m^2\omega^2}{2h^2}$$

$$\alpha = \frac{m\omega}{2h}$$

Then the energy is obtained from

$$E(\alpha_{\min}) = \frac{h^2}{2m}\frac{m\omega}{2h} + \frac{m\omega^2}{8}\frac{2h}{m\omega} = \frac{h\omega}{2} = E_0$$

In this case, the exact ground state energy is obtained because we assumed the correct functional form for the trial wave function. Thus, the ground state wavefunction is clearly given by

$$\psi_0(x) = \left(\frac{m\omega}{\pi h}\right)^{1/4} e^{-m\omega x^2/2\hbar}$$

- Reference:
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- Perturbation theory note by Chris-Kriston kylaris
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