Computational Methods for Quantum Mechanics

Branislav K. Nikolić

Department of Physics and Astronomy, University of Delaware, U.S.A.

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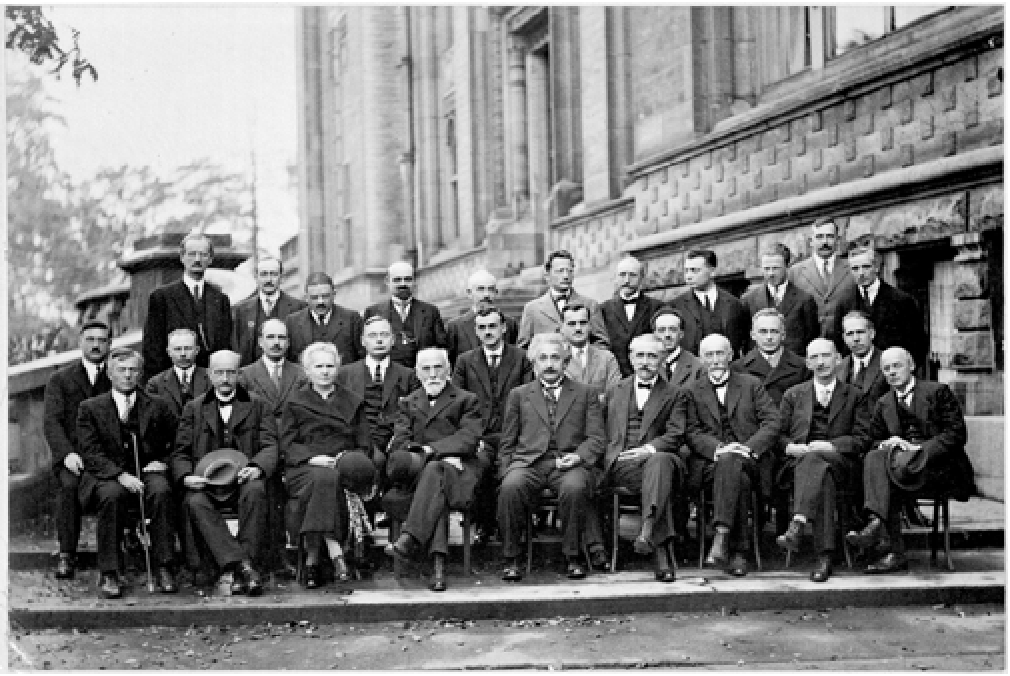
http://www.physics.udel.edu/~bnikolic/teaching/phys660/phys660.html

What is Quantum Mechanics?

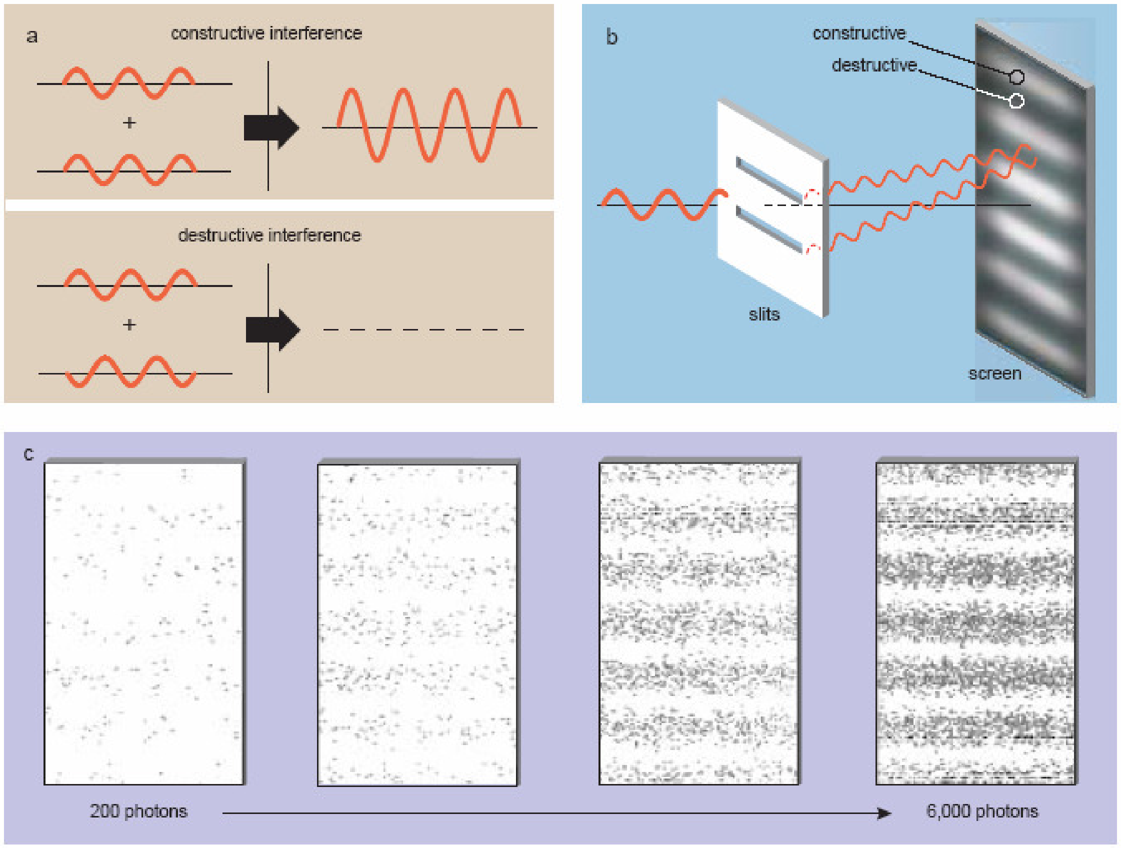
- **Albert Einstein**: "Quantum mechanics is very impressive. But an inner voice tells me that it is not yet the real thing. The theory produces a good deal but hardly brings us closer to the secret of the Old One. I am at all events convinced that He does not play dice."

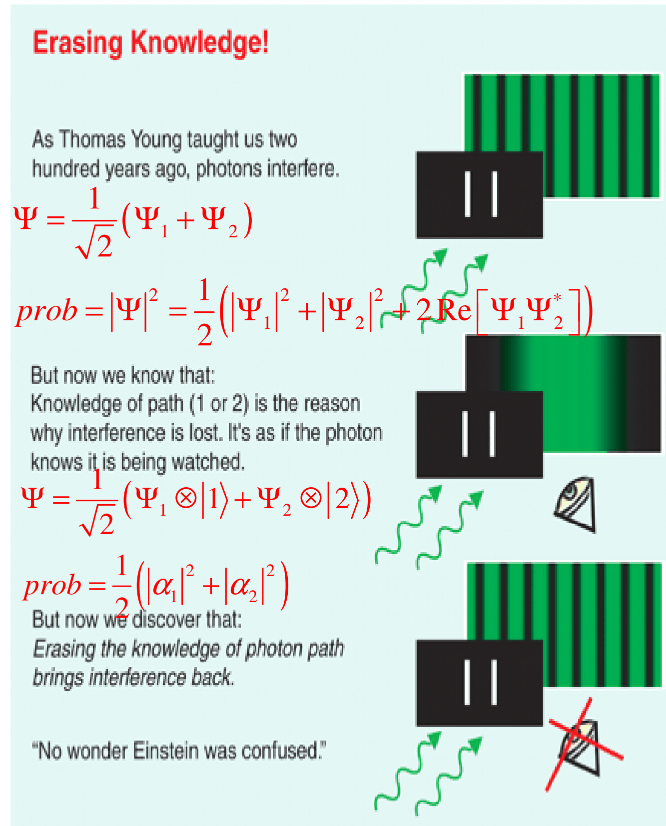


- **Niels Bohr:** "Anyone who is not shocked by quantum theory has not understood a single word."
- **Werner Heisenberg:** "I myself . . . only came to believe in the uncertainty relations after many pangs of conscience. . . "
- **Erwin Schrödinger**: "Had I known that we were not going to get rid of this damned quantum jumping, I never would have involved myself in this business!"

- Groucho Marx: "Very interesting theory - it makes no sense at all."

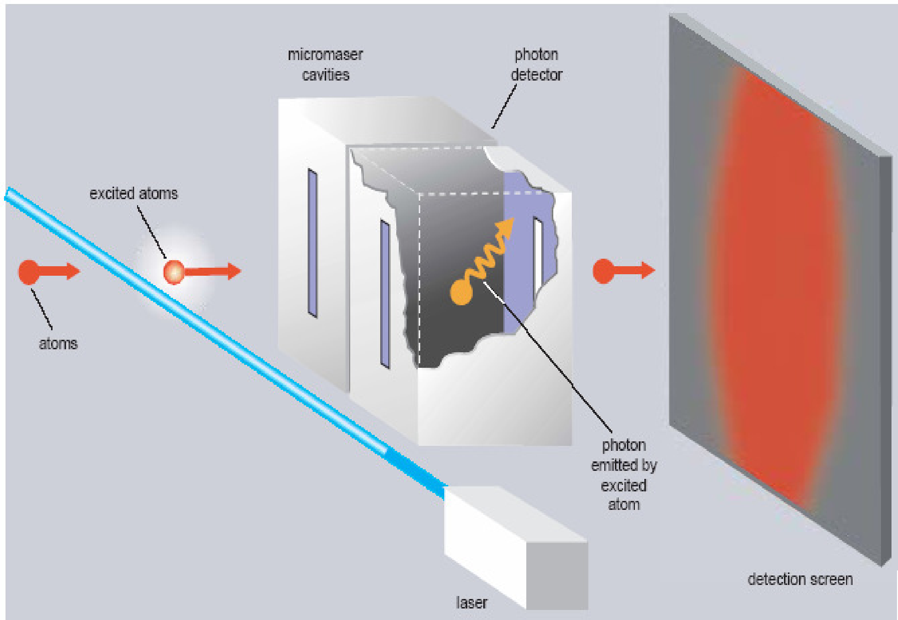
Quantum Interference in Two-Slit Experiments





- The **self interference of individual particles** is the greatest mistery in quntum physics; in fact, Richard Feynman pronounced it **"the only mystery" in quantum theory.**

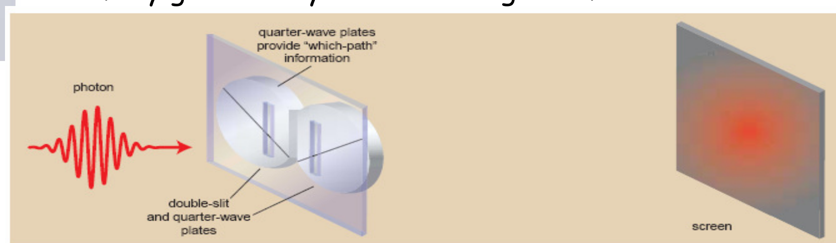
Quantum Erasure

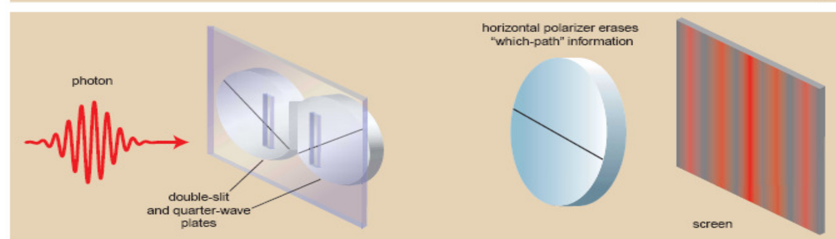


B. Green, *Fabric of Cosmos* (page 149): "These experiments are a magnificent affront to our conventional notions of space and time. Something that takes place long after and far away from something else nevertheless is vital to our description of that something else. By any classical-common sense-reckoning, that's, well, crazy. Of course, that's the point: classical reckoning is the wrong kind of reckoning to use in a quantum universe.... For a few days after I learned of these experiments, I remember feeling elated. I felt I'd been given a glimpse into a veiled side of reality. Common experience—mundane, ordinary, day-to-day activities—suddenly seemed part of a classical charade, hiding the true nature of our quantum world. The world of the everyday suddenly seemed nothing but an inverted magic act, lulling its audience into believing in the usual, familiar conceptions of space and time, while the astonishing truth of quantum reality lay carefully guarded by nature's sleights of hand."

$$|\Psi_0\rangle = \frac{1}{\sqrt{2}}\left(|\text{path }1\rangle|\nwarrow\rangle + |\text{path }2\rangle|\nearrow\rangle\right)$$

$$|\Psi_0\rangle = \frac{1}{2}\left(|\text{path }1\rangle + |\text{path }2\rangle\right)|\rightarrow\rangle + \frac{1}{2}\left(|\text{path }1\rangle - |\text{path }2\rangle\right)|\uparrow\rangle$$





The Canon of Quantum "Churches" Living in Hilbert Space

1. For every system there is a complex **Hilbert space:**

$$\left|\Psi_1\right\rangle, \left|\Psi_2\right\rangle \in H \Rightarrow \alpha\left|\Psi_1\right\rangle + \beta\left|\Psi_2\right\rangle \in H$$

$$\left|\Psi_n\right\rangle \in H \Rightarrow \lim_{n\to\infty}\left|\Psi_n\right\rangle \in H$$

"Wave-particle" duality!

2. States of the system are unit vectors in this space (or, more properly, 1-dim subspaces of H, or projection operators onto H).

$$\left\langle\Psi\middle|\Psi\right\rangle = 1, \text{ i.e., } e^{i\phi}\left|\Psi\right\rangle \subset H, \text{ or } \hat{\rho} = \left|\Psi\right\rangle\left\langle\Psi\right|$$

3. Those things that are observable somehow correspond to **Hermitian operators** $\hat{A}^\dagger = \hat{A} \Leftrightarrow \left\langle\Psi\middle|A\middle|\Phi\right\rangle = \left\langle\Phi\middle|A\middle|\Psi\right\rangle^*$ and their eigenprojectors:

$$\hat{A} = \sum_n a_n \hat{P}_n + \int_p^t s\hat{P}_s ds = \sum_n a_n \left|n\right\rangle\left\langle n\right| + \int_p^t s\left|s\right\rangle\left\langle s\right| ds$$

$$\boxed{\left\langle\hat{A}\right\rangle = \left\langle\Psi\middle|\hat{A}\middle|\Psi\right\rangle = \sum_n a_n \cdot \text{prob}\left(a_n, \hat{A}, \Psi\right)}$$

$$\text{prob}\left([a,b], \hat{A}, \Psi\right) = \left\langle\Psi\middle|\hat{P}_{[a,b]}(\hat{A})\middle|\Psi\right\rangle, \quad \hat{P}_{[a,b]}(\hat{A}) = \sum_{a_n\in[a,b]}\left|n\right\rangle\left\langle n\right|$$

4. Isolated systems evolve according to the Schrödinger equation ...

Four Nobel Truths About Quantum States (Schrödinger 1935)

- **Superposition:** A quantum state is described by a linear superpositions of the basic states.

- **Interference:** The result of measurement depends on the relative phases of the amplitudes in the superpositions.

- **Entanglement:** Complete information about the state of the whole system does not imply complete information about its parts.

- **Nonclonability and uncertainty:** An unknown quantum state can be neither cloned nor observed without being disturbed $\Longrightarrow$ There can be no Quantum Copier Machine that would perform do the following:

$$U_{QCM} : |\Psi\rangle_{\text{original}} \otimes |\Phi\rangle_0 \rightarrow |\Psi\rangle_{\text{original}} \otimes |\Psi\rangle_{\text{original}}$$

Representation of Quantum Mechanics

- Coordinate Representation:

$$|\Psi\rangle = \int |x\rangle\langle x|\Psi\rangle dx = \int \Psi(x)|x\rangle dx$$

- Momentum Representation:

$$|\Psi\rangle = \int |p\rangle\langle p|\Psi\rangle dp = \int |p\rangle\langle p|x\rangle\langle x|\Psi\rangle dpdx$$

$$\langle p|x\rangle = \frac{1}{\sqrt{2\pi\hbar}} e^{-ipx/\hbar} \Rightarrow \Psi(p) = \frac{1}{\sqrt{2\pi\hbar}} \int e^{-ipx/\hbar}\Psi(x)dx$$

- Energy representation: $\hat{H}|E_n\rangle = E_n|E_n\rangle$

$$|\Psi\rangle = \sum_n |E_n\rangle\langle E_n|\Psi\rangle = \sum_n \Psi_n|E_n\rangle$$

Quantum-Mechanical Probabilities in Practice

- Probability to find **coordinate** of a particle in $[x, x+dx]$

$$\langle\Psi|x\rangle\langle x|\Psi\rangle dx = \Psi^*(x)\Psi(x)dx \Rightarrow \int_{-\infty}^{+\infty}\Psi^*(x)\Psi(x)dx = 1$$

$$\hat{x}|x\rangle = x|x\rangle, \quad \Psi^*(x)\Psi(x) = |\Psi(x)|^2$$

- Probability to find **momentum** of a particle in $[p, p+dp]$

$$\langle\Psi|p\rangle\langle p|\Psi\rangle dp = \Psi^*(p)\Psi(p)dp \Rightarrow \int_{-\infty}^{+\infty}\Psi^*(p)\Psi(p)dp = 1$$

$$\hat{p}|p\rangle = p|p\rangle, \quad \Psi^*(p)\Psi(p) = |\Psi(p)|^2$$

- Probability to find **energy** of a particle to be E_n

$$\langle\Psi|E_n\rangle\langle E_n|\Psi\rangle = |\langle E_n|\Psi\rangle|^2 = \Psi^*{}_n\Psi_n \Rightarrow \sum_n \Psi^*{}_n\Psi_n = 1$$

Schrödinger Equation(s)

- Time Evolution of state vectors

$$\boxed{i\hbar \frac{d\left|\Psi\right\rangle}{dt} = \hat{H}\left|\Psi\right\rangle \Rightarrow \text{stationary: } \hat{H}\left|\Psi\right\rangle = E\left|\Psi\right\rangle}$$

- Time evolution of coordinate wave functions for a single particle acted on by a conservative force with potential $V(\mathbf{x})$

$$i\hbar \frac{\partial \Psi(\mathbf{x})}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2 \Psi(\mathbf{x}) + V(\mathbf{x})\Psi(\mathbf{x})$$

- Momentum representation for a single particle of mass *m* acted on by a conservative force with potential $V(x) \Rightarrow V(p) = \frac{1}{2\pi\hbar}\int V(x) e^{-ipx/\hbar} dx$

$$i\hbar \frac{\partial \Psi(\mathbf{p})}{\partial t} = \frac{\mathbf{p}^2}{2m}\Psi(p) + \int_{-\infty}^{+\infty} V(\mathbf{p}-\mathbf{p}')\Psi(\mathbf{p}')d\mathbf{p}'$$

Pictures of Quantum Mechanics

$$\left\langle \hat{A} \right\rangle(t) = \left\langle \Psi \middle| \hat{A} \middle| \Psi \right\rangle = \begin{pmatrix} \Psi_1^* & \Psi_2^* & \ldots & \Psi_N^* \end{pmatrix} \mathbf{A} \begin{pmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_N \end{pmatrix}$$

Schrödinger

$$\left\langle \hat{A} \right\rangle(t) = \left\langle \hat{U}\Psi \middle| \hat{A}(t) \middle| \hat{U}\Psi \right\rangle$$

$$= \left\langle \Psi(t) \middle| \hat{A} \middle| \Psi(t) \right\rangle$$

Heinseberg

$$\left\langle \hat{A} \right\rangle(t) = \left\langle \Psi \middle| \hat{U}^\dagger \hat{A} \hat{U} \middle| \Psi \right\rangle$$

$$= \left\langle \Psi \middle| \hat{A}(t) \middle| \Psi \right\rangle$$

Dirac

$$\left\langle \hat{A} \right\rangle(t) = \left\langle \hat{U}_0\Psi \middle| \hat{U}_1^\dagger \hat{A} \hat{U}_1 \middle| \hat{U}_0\Psi \right\rangle$$

$$= \left\langle \Psi(t) \middle| \hat{A}(t) \middle| \Psi(t) \right\rangle$$

Heisenberg Uncertainty (Indeterminacy) Relations

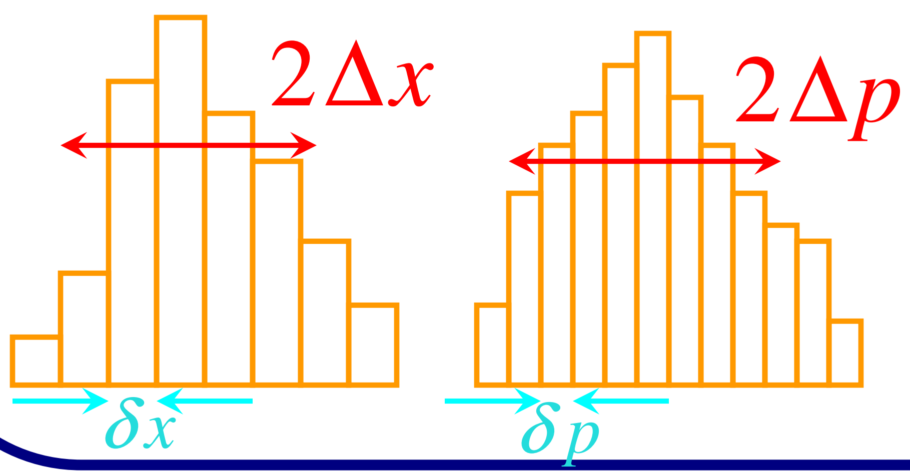
- Operators (of course, Hermitian), which represent physical quantities in QM, in general, do not commute:

$$\left[\hat{A},\hat{B}\right]=\hat{A}\cdot\hat{B}-\hat{B}\cdot\hat{A}\neq 0\Rightarrow \Delta\hat{A}\Delta\hat{B}\geq\frac{1}{2}\left|\left\langle\left[\hat{A},\hat{B}\right]\right\rangle\right|$$

$$\left(\Delta\hat{A}\right)^2=\left\langle\left(\hat{A}-\left\langle\hat{A}\right\rangle\right)^2\right\rangle=\left\langle\hat{A}^2\right\rangle-\left\langle\hat{A}\right\rangle^2\Rightarrow\Delta\hat{A}=0\text{ iff }\hat{A}\left|\Psi\right\rangle=a\left|\Psi\right\rangle$$

- Coordinate and momentum are c-numbers $xp-px=0$ in classical physics, but in QM:

$$\boxed{\left[\hat{x},\hat{p}_x\right]=i\hbar\Rightarrow\Delta\hat{x}\Delta\hat{p}_x\geq\frac{\hbar}{2}}$$

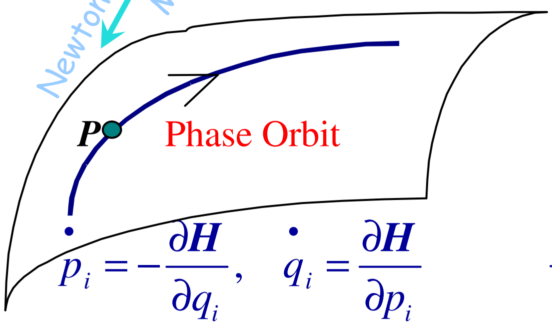


- The experimental test of the Heisenberg inequality **does not involve** simultaneous measurements of **x** and **p**, but rather it involves the measurement of one or the other of these dynamical variables on each independently prepared representative of the particular state $\left|\Psi\right\rangle$ being studied.

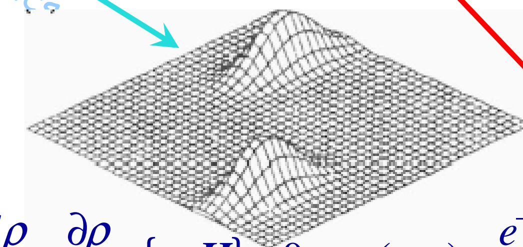
Classical vs. Quantum Mechanics

Newton-Lagrange-Hamilton Mechanics

Boltzmann-Gibbs Statistical Mechanics



$$\dot{p}_i = -\frac{\partial H}{\partial q_i}, \quad \dot{q}_i = \frac{\partial H}{\partial p_i}$$



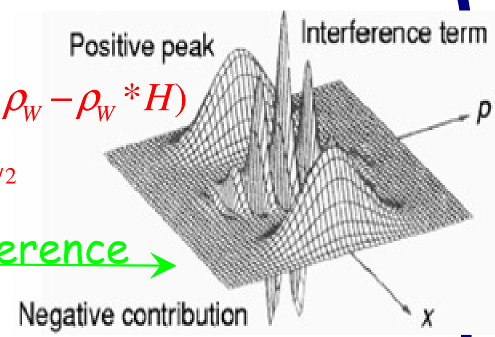
$$\frac{d\rho}{dt} \equiv \frac{\partial \rho}{\partial t} + \{\rho, H\} = 0 \Rightarrow \rho(p,q) = \frac{e^{-\beta H(p,q)}}{Z}$$

$$\rho_W(q,p)$$

$$\frac{\partial \rho_W}{\partial t} = \frac{1}{i\hbar}(H * \rho_W - \rho_W * H)$$

$$* \equiv e^{i\hbar(\overleftarrow{\partial}_q \overrightarrow{\partial}_p - \overleftarrow{\partial}_p \overrightarrow{\partial}_q)/2}$$

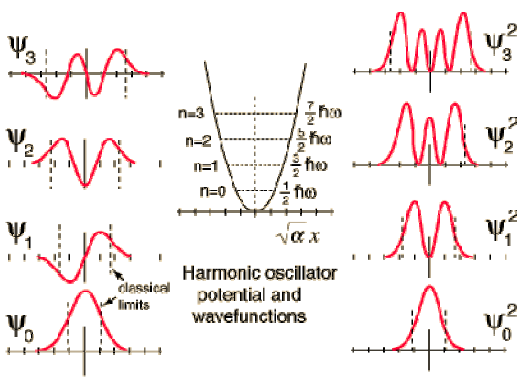
decoherence



Moyal-Groenewald-Weyl Deformation Quantization

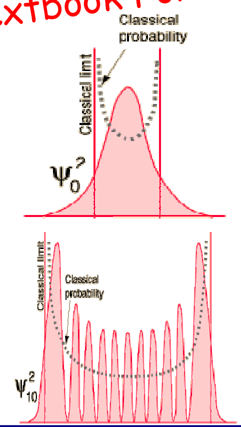
Dirac-Heisenberg-Schrödinger Textbook Formulation in Hilbert Space

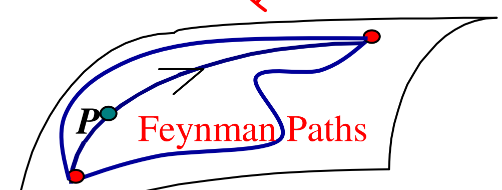
Feynman-Dirac Path Integral



$$\Psi(q), \hat{A}$$

$$i\hbar \frac{d\hat{A}}{dt} = \frac{\partial \hat{A}}{\partial t} + [\hat{A}, \hat{H}]$$





$$K(q_f, t_f \leftarrow q_i, t_i) = \int Dq(t) e^{iS[q]/\hbar}$$

Quantum Tunneling Through Single Barrier in Solid State Systems

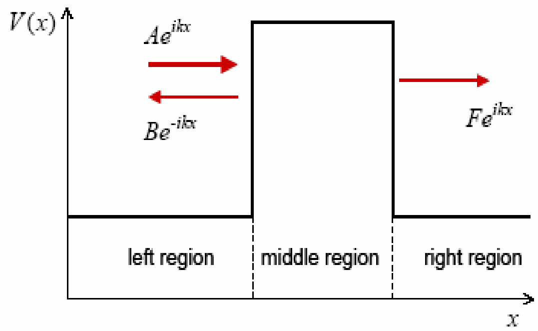


Figure 1.3: Simple approximation of the potential along the transport direction of a tunnel junction, see Fig. 1.2. In the metal (left and right regions) the potential is constant, $V(x) = V_1$. In the insulator the potential is also constant, $V(x) = V_0$, where $V_0 > V_1$. The incoming, reflected and transmitted waves are given by Ae^{ikx}, Be^{-ikx} and Fe^{ikx}.

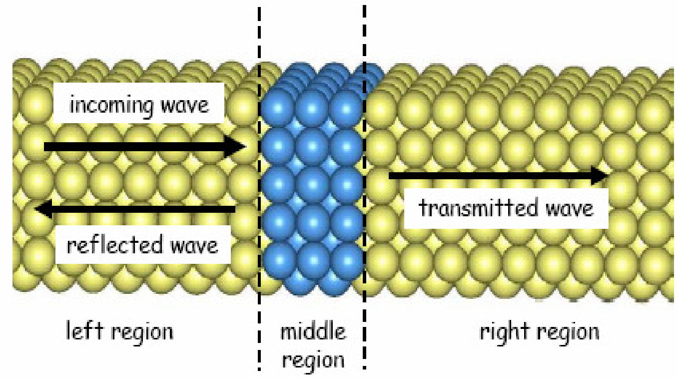
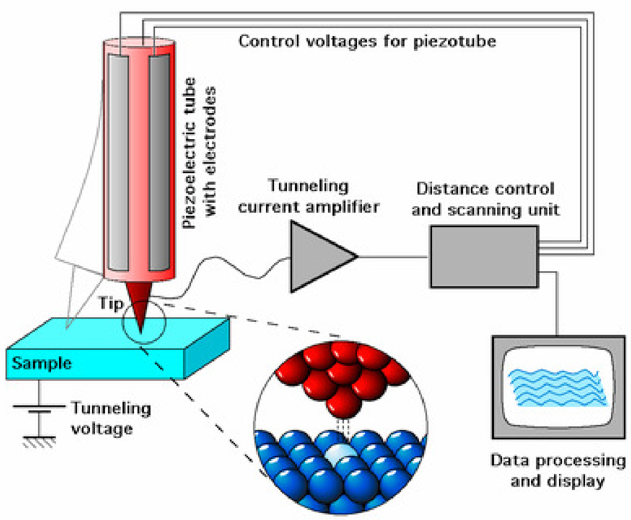
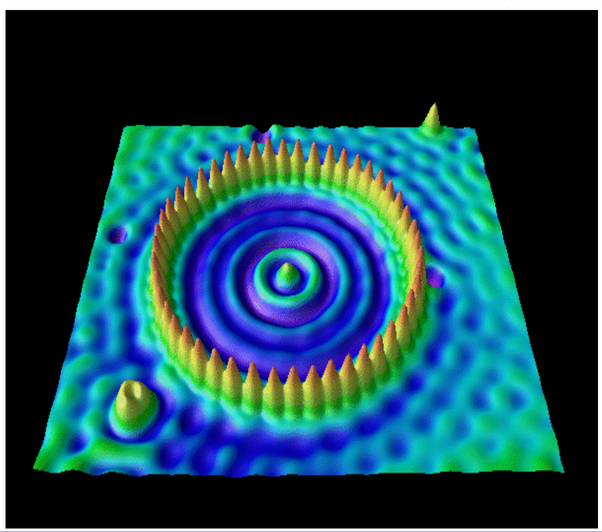
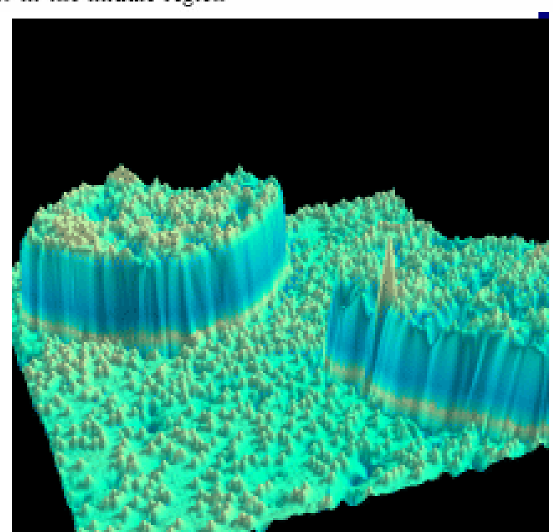


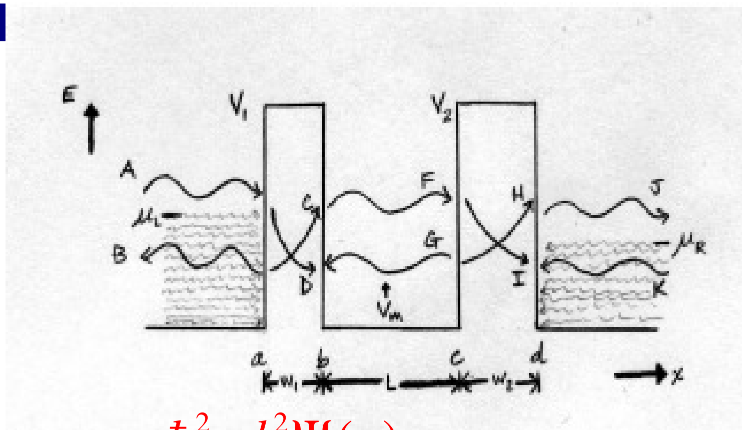
Figure 1.2: Schematic representation of a tunnel junction. The yellow balls represent atoms of a metal, the blue balls represent atoms of an insulator. The left and right regions stretch macroscopically far into the left and right, respectively. The electron waves in the metal are reflected or transmitted by the insulator in the middle region







Quantum Tunneling Through Double Barrier in Textbooks



$$-\frac{\hbar^2}{2m}\frac{d^2\Psi(x)}{dx^2} = (E-V)\Psi(x)$$

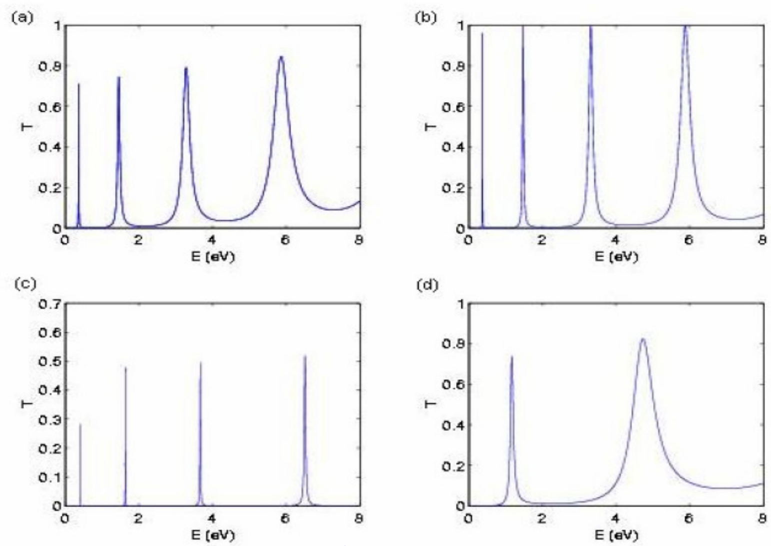
$$\Psi(x) = \begin{cases} Ae^{ikx} + Be^{-ikx}, x < a \\ Ce^{qx} + De^{-qx}, a < x < b \\ Fe^{ik_m x} + Ge^{-ik_m x}, b < x < c \\ He^{px} + Ie^{-px}, c < x < d \\ Je^{ikx} + Ke^{-ikx}, x > d \end{cases}$$

$$k = \sqrt{\frac{2mE}{\hbar^2}}, \quad q = \sqrt{\frac{2m(V_1 - E)}{\hbar^2}}$$

$$k_m = \sqrt{\frac{2m(E - V_m)}{\hbar^2}}, \quad p = \sqrt{\frac{2m(V_2 - E)}{\hbar^2}}$$

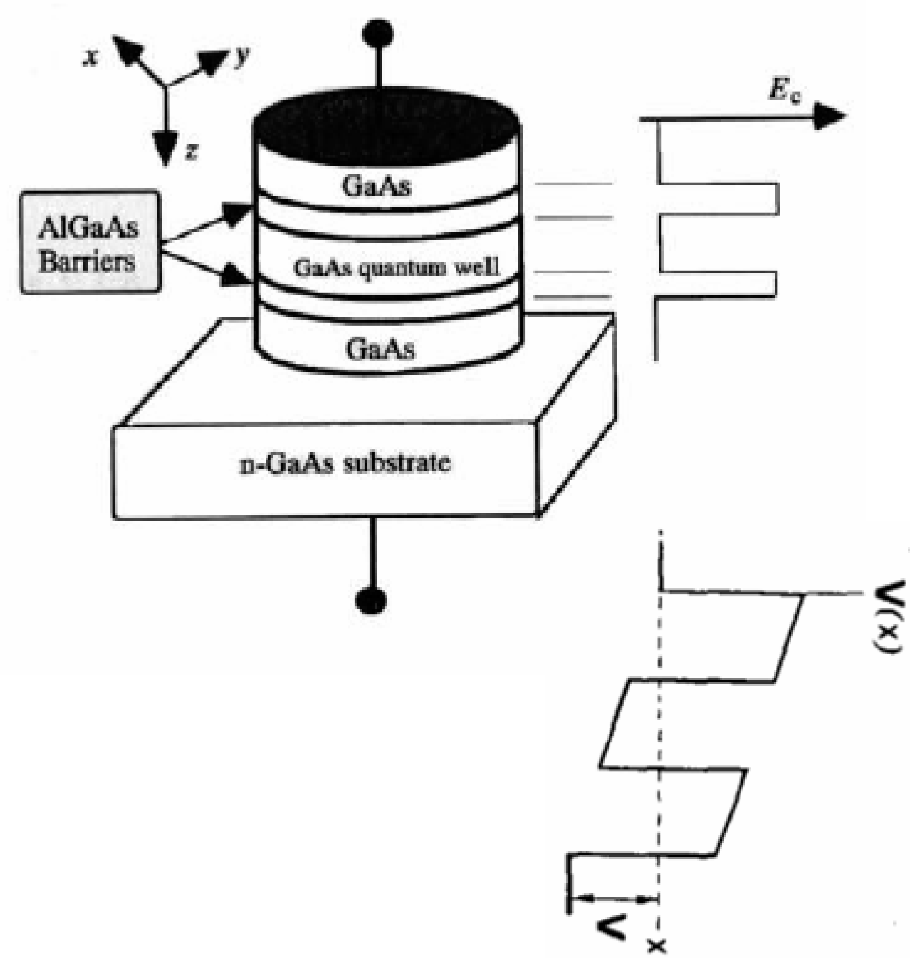
$$j_x = \frac{\hbar}{2mi}\left(\Psi^*(x)\frac{\partial\Psi(x)}{\partial x} - \Psi(x)\frac{\partial\Psi^*(x)}{\partial x}\right)$$

$$T = \frac{j_{transmitted, x>d}}{j_{incident, x<a}} = \begin{cases} \frac{|H|^2}{|A|^2}, \text{ for electrons incident from the left } (+k \text{ states}) \\ \frac{|B|^2}{|K|^2}, \text{ for electrons incident from the right } (-k \text{ states}) \end{cases}$$



Transmission probability versus incident energy for: **(a)** asymmetric barriers; **(b)** symmetric barriers; **(c)** tall barriers; and **(d)** narrow well.

Quantum Tunneling Through Double Barrier in Solid State Systems



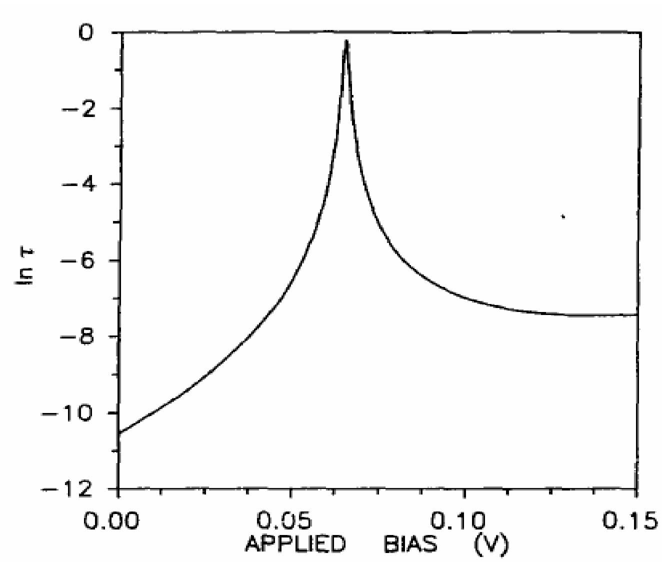


Fig. 3. Transmission coefficient obtained numerically as a function of the applied voltage in a double barrier heterostructure. The potential barrier is 0.25 eV height, $L=3d=150$ Å and the energy of the incident electron is 50 meV.

Plane Wave Solutions of the Free Particle Schrödinger Equation

- Plane waves solve the **free particle** Schrödinger equation:

$$i\hbar \frac{\partial}{\partial t}\Psi_p(t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi_p(x,t)$$

$$\Psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}}\exp\left[-\frac{i}{\hbar}(Et - px)\right], E = \frac{p^2}{2m}$$

$$\underbrace{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}}_{\hat{H}}\underbrace{\frac{1}{(2\pi\hbar)^{1/2}}e^{\frac{i}{\hbar}px}}_{|E\rangle} = \underbrace{\frac{p^2}{2m}}_{E}\underbrace{\frac{1}{(2\pi\hbar)^{1/2}}e^{\frac{i}{\hbar}px}}_{|E\rangle}$$

Gaussian Wave Packet: Construction

$$\Psi_p(x) = \frac{1}{(2\pi\hbar)^{1/2}} \exp\left[-\frac{i}{\hbar}(Et - px)\right], \; E = \frac{p^2}{2m}$$

- **Linear superpositions** of plane waves are also solutions!

$$\Psi(x,t) = \sum_n w_n \Psi_p(x,t) \rightarrow \Psi(x,t) = \int_{-\infty}^{+\infty} f(p)\Psi_p(x - x_0, t)\,dp$$

- For Gaussian wave packet use Gaussian spectral function:

$$f(p) = \frac{1}{(2\pi)^{1/4}\sqrt{\sigma_p}} \exp\left[-\frac{(p-p_0)^2}{4\sigma_p^2}\right]$$

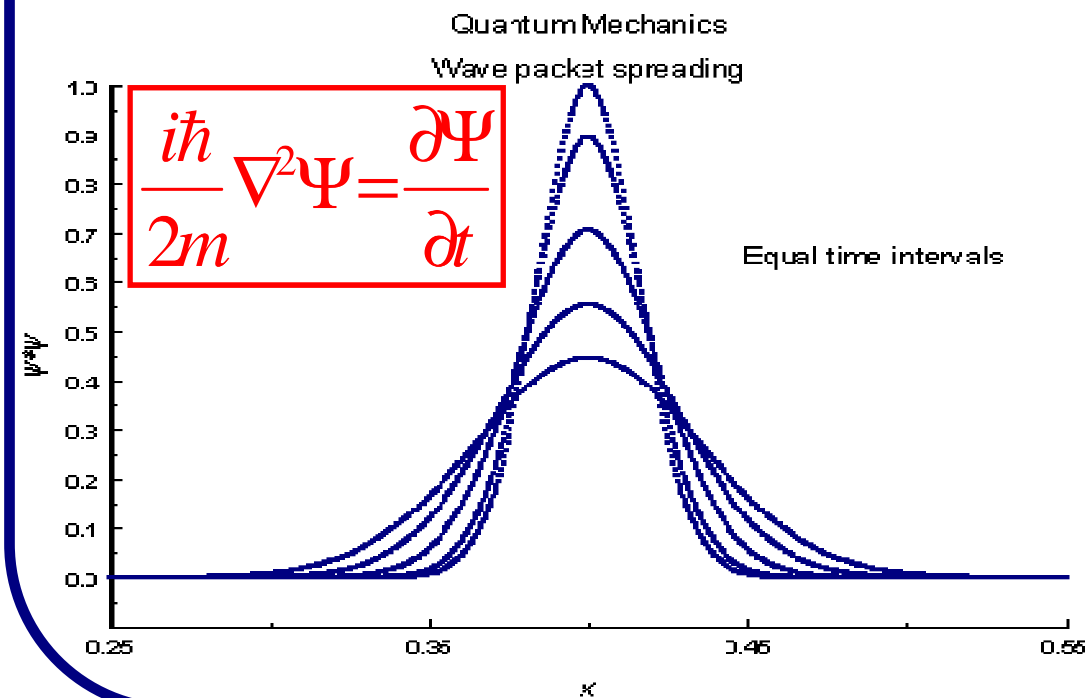
Spreading of Gaussian Wave Packet at Rest

- The probability density that the particle is located at some location in space is determined from the wave function (in coordinate representation):

$$\rho(\mathbf{x}) = \Psi^*(\mathbf{x})\Psi(\mathbf{x}) = \langle \Psi | \mathbf{x} \rangle \langle \mathbf{x} | \Psi \rangle$$

- For a free particle $V(\mathbf{x})=0$ the Schrödinger equation has the form of a diffusion equation with diffusion coefficient $i\hbar/2m$.

$$\boxed{\frac{i\hbar}{2m}\nabla^2\Psi = \frac{\partial \Psi}{\partial t}}$$



As time progresses the width of the distribution increases $\propto (\hbar t/m)^{1/2}$. This width is proportional to the standard deviation of the position x. In quantum mechanics the standard deviation of the probability distribution of a variable is often called the uncertainty in the variable. If we have an object of mass 1 kg then the time scale for the uncertainty in the position of this object to increase by about $10^{-6}\,m$ is estimated to be $3 \cdot 10^6$ years. Hence classical physics is amply adequate to describe the dynamics of macroscopic objects.

Moving Gaussian Wave Packet

$$\Psi(x,t) = \int_{-\infty}^{+\infty} f(p)\Psi_p(x-x_0,t)dp = M(x,t)e^{i\phi(x,t)}$$

$$\text{amplitude function}: M(x,t) = \frac{1}{(2\pi)^{1/4}\sqrt{\sigma_p}}\exp\left[-\frac{(x-x_0-v_0t)^2}{4\sigma_x^2}\right]$$

$$\text{phase}: \phi(x,t) = \frac{1}{\hbar}\left[p_0 + \frac{\sigma_p^2}{\sigma_x^2}\frac{t}{2m}(x-x_0-v_0t)\right](x-x_0-v_0t) + \frac{p_0}{2\hbar}v_0t - \frac{\arctan\frac{2\sigma_p^2 t}{\hbar m}}{2}$$

$$\text{group velocity}: v_0 = \frac{p}{m} \qquad \text{localization in space}: \sigma_x^2 = \frac{\hbar^2}{4\sigma_p^2}\left(1 + \frac{4\sigma_p^2}{\hbar^2}\frac{t^2}{m^2}\right)$$

- Physical **(i.e., measurable)** properties are contained in:

$$\boxed{\rho(x,t) = \Psi(x,t)\Psi^*(x,t) = \frac{1}{\sqrt{2\pi}\sigma_x(t)}\exp\left[-\frac{(x-\langle x(t)\rangle)^2}{2\sigma_x^2}\right]}$$

$$\boxed{\langle \hat{x} \rangle = \int_{-\infty}^{+\infty} \Psi(x,t)x\Psi^*(x,t) = x_0 + v_0 t}$$

Gaussian Wave Packet: Uncertainty Relations

$$\mathrm{var}(\hat{x}) = \left\langle \left(\hat{x} - \langle \hat{x} \rangle\right)^2 \right\rangle = \int_{-\infty}^{+\infty} \Psi(x,t)\left(\hat{x} - \langle \hat{x} \rangle\right)^2 \Psi^*(x,t)dx = \sigma_x^2$$

$$\mathrm{var}(\hat{p}) = \left\langle \left(\hat{p} - \langle \hat{p} \rangle\right)^2 \right\rangle = \int_{-\infty}^{+\infty} \Psi(x,t)\left(\frac{\hbar}{i}\frac{\partial}{\partial x} - p_0\right)^2 \Psi^*(x,t)dx = \sigma_p^2$$

$$\boxed{\Delta\hat{x}\Delta\hat{p} = \sqrt{\mathrm{var}(\hat{x})}\sqrt{\mathrm{var}(\hat{p})} = \sigma_x(t)\sigma_p \geq \frac{\hbar}{2}}$$

$$t = 0 \Rightarrow \begin{cases} \Psi(x,0) = M(x,0)e^{i\phi(x,0)} = \dfrac{1}{(2\pi)^{1/4}\sqrt{\sigma_x}}\exp\left[-\dfrac{(x-x_0)^2}{4\sigma_x^2}\right]\exp\left[\dfrac{i}{\hbar}p_0(x-x_0)\right] \\ \Delta\hat{x}\Delta\hat{p} = \sigma_x(t=0)\sigma_p = \dfrac{\hbar}{2\sigma_p}\sigma_p = \dfrac{\hbar}{2} \quad \leftarrow \text{minimum uncertainty state} \end{cases}$$

Time-Dependent Schrödinger Equation: Direct Solution

- The time dependent Schrödinger equation can be compactly written a

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi, \quad \hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})$$

where we assume Hamiltonian for a single particle in a potential $V(\mathbf{r})$.

- Lets try to use **naïve Euler method** to convert this into a difference equation:

$$\Psi^{n+1} = \Psi^n - \frac{i\Delta t}{\hbar}\hat{H}\Psi^n$$

Where the superscript represent time and Δt is the time increment.

- The **second derivative** in the Hamiltonian is approximated by:

$$\boxed{\left.\frac{\partial^2 \Psi^n}{\partial x^2}\right|_k \simeq \frac{\Psi^n_{k+1} - 2\Psi^n_k + \Psi^n_{k-1}}{\Delta x^2}}$$

where Δx is the interval in x, with similar expressions for the contributions from the y and z coordinates.

Stability Problem of Direct Euler Approach

- This finite difference equation is **unstable** - consider the case of a free particle in one dimension:

$$\Psi_k^{n+1} = \Psi_k^n + iQ\left(\Psi_{k+1}^n - 2\Psi_k^n + \Psi_{k-1}^n\right),\ Q = \frac{\hbar\Delta t}{2m\Delta x^2}$$

- This is a **linear second order difference equation** in two variables. We can solve it by Fourier analysis in the x direction. What this means is that x-dependence can be taken to be a superposition of solutions of form e^{ikx}:

$$\left.\begin{array}{l} \Psi_k^n = \zeta^n \exp\left(i\kappa k\Delta x\right) \\ x = k\Delta x + \text{a constant} \end{array}\right\} \Rightarrow \zeta^{n+1} = \zeta^n + iQ\left[\exp\left(i\kappa\Delta x\right) - 2 + \exp\left(-i\kappa\Delta x\right)\right]\zeta^n$$

$$\zeta^{n+1} = \zeta^n\left[1 - 2iQ\left(1 - \cos(\kappa\Delta x)\right)\right]$$

- Thus, at each time step ζ is multiplied by the **amplification factor**:

$$\alpha = 1 - 2iQ\left[1 - \cos\left(\kappa\Delta x\right)\right] \Leftrightarrow |\alpha| = \sqrt{1 + 4Q^2\left[1 - \cos\left(\kappa\Delta x\right)\right]^2}$$

$$\exists\,\kappa \Rightarrow |\alpha| > 1 \text{ for } Q > 0$$

Analogous Stability Problem in Diffusion Equation

- Diffusion equation can be maped onto the Schrödinger equation in "imaginary time", and vice versa → similar analysis of stability of the Euler method leads to:

$$\alpha = 1 - 2Q\left[1 - \cos\left(\kappa \Delta x\right)\right], Q = \frac{D\Delta t}{\Delta x^2}$$

- In this case the diffusion coefficient is a real number and the amplification factor is also real. Here D is the **diffusion coefficient**.

- The **stability criterion** which imposes restriction on the time step is:

$$\boxed{|\alpha| < 1 \text{ if } 4Q < 1 \Rightarrow \Delta t < \frac{\Delta x^2}{4D}}$$

Implicit Method Cure?

- The instability of the Euler method is cured by **time-reversal**, i.e., we can use the implicit method. For the free particle:

$$\Psi_k^{n+1} = \Psi_k^n + iQ\left(\Psi_{k+1}^{n+1} - 2\Psi_k^{n+1} + \Psi_{k-1}^{n+1}\right), \quad Q = \frac{\hbar \Delta t}{2m\Delta x^2}$$

so that "amplification" factor is now:

$$\boxed{\alpha = \frac{1}{1+2iQ\left[1-\cos\left(\kappa\Delta x\right)\right]} \Rightarrow \left|\alpha\right| = \frac{1}{\sqrt{1+4Q^2\left[1-\cos\left(\kappa\Delta x\right)\right]^2}} \leq 1}$$

- **However, we now have new problem with unitarity:** The implicit method does not preserve **unitarity**, i.e., it does not keep the normalization integral constant. This is related to the fact that the amplification factor has magnitude less than or equal to one.

$$\boxed{\int \Psi(\mathbf{r})^* \Psi(\mathbf{r}) d\mathbf{r} = 1}$$

A Cure for both Stability and Unitarity

- The unitarity problem is cured by using a more accurate method — evaluate the time derivative at the midpoint of the time interval by taking the average of the implicit and explicit Euler methods approximations for the Hamiltonian.
- For free particle such finite difference method yields the equation:

$$\Psi_k^{n+1} = \Psi_k^n + i\frac{Q}{2}\left(\Psi_{k+1}^{n+1} - 2\Psi_k^{n+1} + \Psi_{k-1}^{n+1}\right) + i\frac{Q}{2}\left(\Psi_{k+1}^{n} - 2\Psi_k^{n} + \Psi_{k-1}^{n}\right)$$

$$\alpha = \frac{1 - iQ\left[1-\cos\left(\kappa\Delta x\right)\right]}{1 + iQ\left[1-\cos\left(\kappa\Delta x\right)\right]} \Rightarrow |\alpha| = 1$$

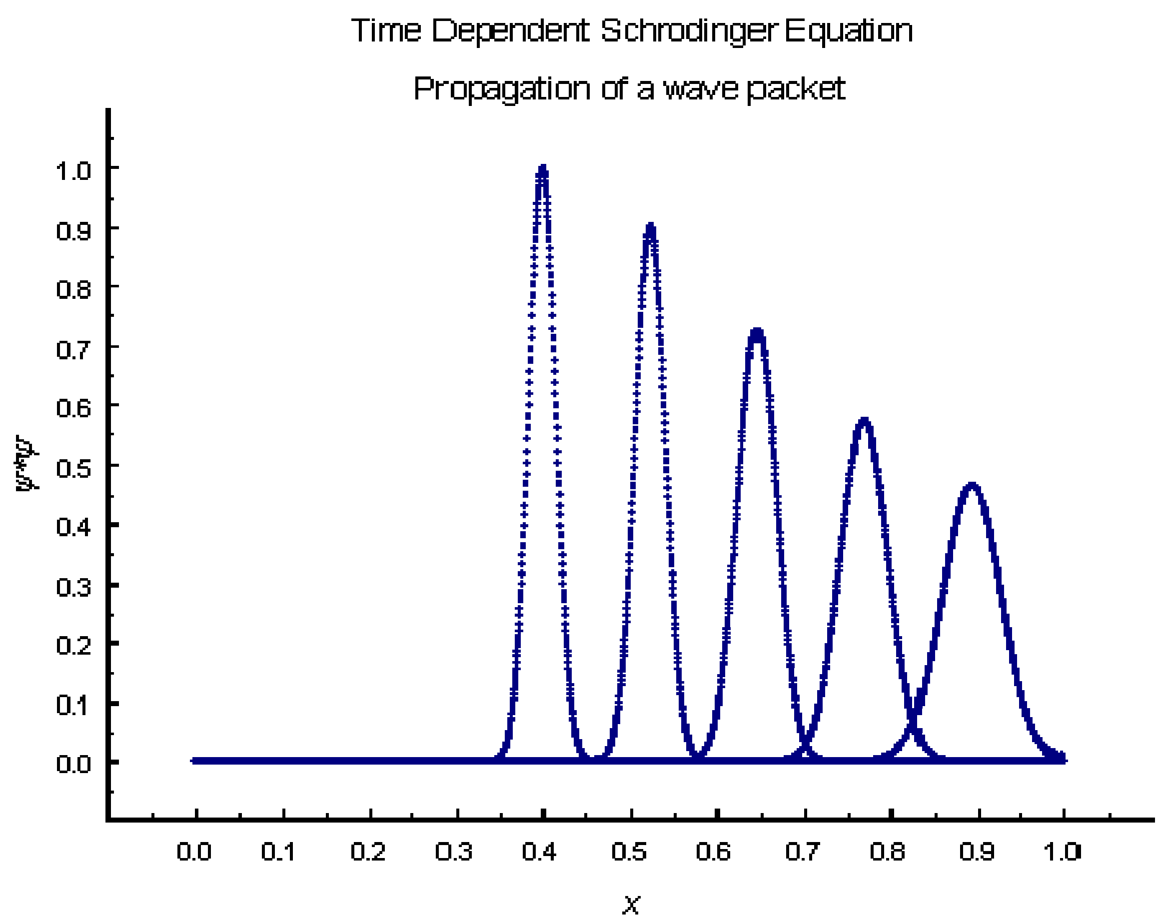
- **This is now finally a stable method that preserves unitarity!**
- For a 1-dim particle in a potential $V(x)$, the finite difference TDSE is:

$$\Psi_k^{n+1} - iq\left(\Psi_{k+1}^{n+1} - 2\Psi_k^{n+1} + \Psi_{k-1}^{n+1}\right) + irV_k\Psi_k^{n+1} = \Psi_k^n + iq\left(\Psi_{k+1}^{n} - 2\Psi_k^{n} + \Psi_{k-1}^{n}\right) - irV_k\Psi_k^n$$

$$V_k = V(x_k),\ q = \frac{Q}{2} = \frac{\hbar\Delta t}{4m(\Delta x)^2},\ r = \frac{\Delta t}{2\hbar}$$

- If considered as a set of linear equations for the unknowns $\Psi_1^{n+1}, \Psi_2^{n+1}, \ldots, \Psi_K^{n+1}$, we have a **tri-diagonal system** of **linear equations** that can be solved much easier than standard LU decomposition + forward-backward substitution. Note, however, that you need to use **complex arithmetic**.

Test Example for Computational Algorithm for Quantum Mechanical Unitary Evolution



- The figure shows the probability distribution at equal time intervals for a Gaussian wave packet propagating to the right.

Solving Time-Independent Schrödinger Equation

- Separation of variables to solve the partial differential equation:

$$\Psi(\mathbf{r},t) = R(\mathbf{r})T(t) \Rightarrow \frac{1}{R}\left[-\frac{\hbar^2}{2m}\nabla^2 R + V(\mathbf{r})R\right] = i\hbar\frac{1}{T}\frac{dT}{dt} = E$$

$$T(t) = \exp\left(-\frac{iEt}{\hbar}\right), \quad -\frac{\hbar^2}{2m}\nabla^2 R + V(\mathbf{r})R = ER$$

- The spatial part has boundary conditions that often lead to an **eigenvalue problem**, i.e., there is a solution for R only for a discrete set of values of E This is formally similar to oscillations in a linear chain. If we label the eigenvalues $E_1, E_2, E_3, \ldots$ and corresponding eigenfunctions $R_1, R_2, R_3, \ldots$ then the complete solution is:

$$\Psi(\mathbf{r},t) = \sum_{l=1}^{\infty} \alpha_l R_l(\mathbf{r}) \exp\left(-\frac{iE_l t}{\hbar}\right)$$

$$|\Psi(t)\rangle = \exp\left(-\frac{i\hat{H}t}{\hbar}\right)|\Psi(0)\rangle = \sum_l \exp\left(-\frac{iE_l t}{\hbar}\right)|l\rangle\langle l|\Psi(0)\rangle$$

The constants α_l are determined from initial conditions at $t = 0$

Variational Methods: Principle

- Consider the functional (here $\Phi(\mathbf{r})$ is any complex function of position):

$$\tilde{E} = \frac{\int \Phi^* \hat{H} \Phi \, d\mathbf{r}}{\int \Phi^* \Phi \, d\mathbf{r}}$$

Theorem: $\tilde{E}$ is stationary if Φ is a solution of $\hat{H}\Psi = E\Psi$ and then:

$$\tilde{E} = E$$

→That is, if we change Φ by a small amount $\delta\Phi$ then to lowest order in $\delta\Phi$, $\tilde{E}$ **does not change**.

Corollary:

$$\boxed{\tilde{E} = \frac{\int \Phi^* \hat{H} \Phi d\mathbf{r}}{\int \Phi^* \Phi d\mathbf{r}} \geq E_{\min}}$$

This is valid for any $\Phi(\mathbf{r})$, where $E_{\min}$ is the lowest (ground) state energy.

Variational Methods: Practice

Theorem: If Φ is an approximate solution to Schrödinger equation and the difference between this and the exact solution Ψ is $\delta\Psi = \Phi - \Psi$, then the difference between the value of the functional and the eigenvalue is

$$\tilde{E} - E = \frac{\int \delta\Psi^* \left(\hat{H} - E\right) \delta\Psi \, d\mathbf{r}}{\int \Psi^* \Psi \, d\mathbf{r}} + \text{higher order terms}$$

- This tells us that the error in the eigenvalue is **quadratic** in the error in the eigenfunction. We use this to develop **variational methods** for solving the Schrödinger equation. One such method is to use a simple function with a few adjustable parameters as a **trial** function:

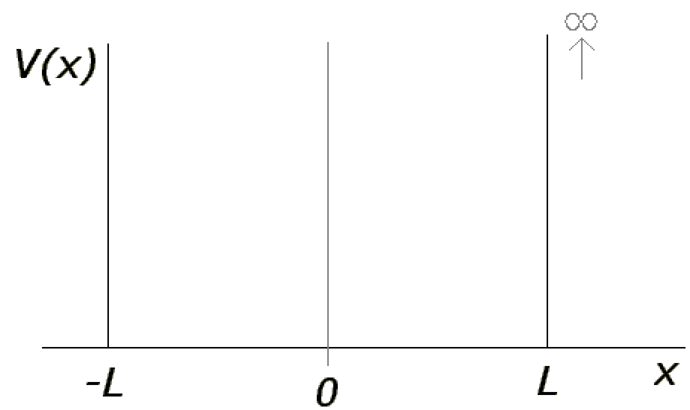
$$\Phi(\mathbf{r}; p_1, p_2, \ldots, p_n)$$

- The functional then depends on the adjustable parameters $p_1, p_2, \ldots, p_n$. Minimizing the functional gives an upper bound to the minimum energy of the system.

Variational Methods: Textbook Example

Consider a particle that is free to move in a one-dimensional box but cannot get out of the box. The walls of the box are at $x = -L$ and $x = L$. The potential for the box is:

$$V(x) = \begin{cases} 0, & |x| < L \\ \infty, & \text{otherwise} \end{cases} \Rightarrow \Psi(\pm L) = 0$$



- **Exact solution:**

$$-\frac{\hbar}{2m}\frac{d^2\Psi}{dx^2} = E\Psi \Rightarrow \Psi = A\exp(\pm ikx),\ k^2 = \frac{2mE}{\hbar^2}$$

$$\Psi_\pm = \begin{cases} A\cos(k_+ x) \\ A\cos(k_- x) \end{cases},\ k = \frac{n\pi}{2L},\ E = \frac{\hbar^2}{2m}\left(\frac{n\pi}{2L}\right)^2 \Rightarrow E_{\min} = \frac{\pi^2\hbar^2}{8mL^2} = 1.2337\frac{\hbar^2}{mL^2}$$

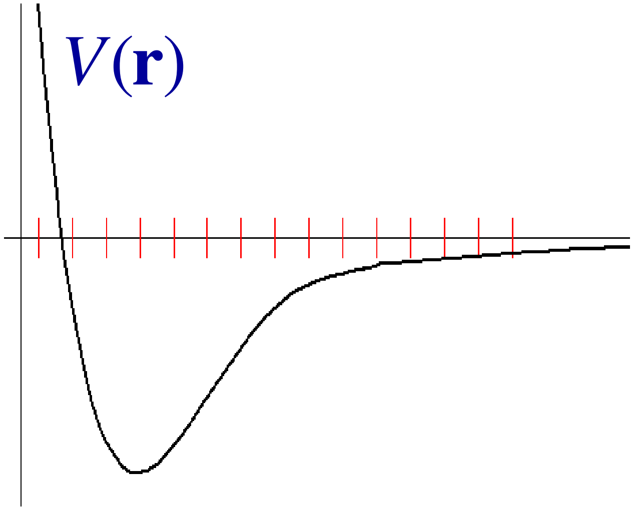
- Trial function for the **variational** method: $\Phi = 1 - \left(\frac{x}{L}\right)^2 \text{ iff } |x| < L$

$$\int_{-L}^{L}\Phi^*\hat{H}\Phi dx = \int_{-L}^{L}\left[1-\left(\frac{x}{L}\right)^2\right]\frac{\hbar}{mL^2}dx = \frac{4}{3}\frac{\hbar^2}{mL},\quad \int_{-L}^{L}\Phi^*\Phi dx = \frac{16}{15}L$$

$$\boxed{E = \frac{4\hbar^2/3mL}{16L/15} = 1.25\frac{\hbar^2}{mL^2}}$$

Variational Methods Through Computation: Quantum Monte Carlo

- This is a variational method that uses a **Monte Carlo** technique to adjust an initial guess for the eigenfunction in such a way as to minimize the functional for the energy eigenvalue.



We choose a range in x and divide this range into K grid points. Outside this range we make the approximation that the wave function is zero. This is equivalent to putting the system inside a box. By varying the location of the walls of the box, you can test how the solution depends on this approximation.

- Replace the 2nd order derivative by a finite-difference on the grid so that at the **k-th** point:

$$\left(\hat{H}\Phi\right)_k = -\frac{\hbar^2}{2m}\left[\frac{\Phi_{k+1} - 2\Phi_k + \Phi_{k-1}}{(\Delta x)^2}\right] + V(x_k)\Phi_k$$

Quantum Monte Carlo: Part II

- Replace continous integrals by trapezoidal (or Simpson) rule-generated discrete sums:

$$I = \int_0^\infty \Phi^* \hat{H} \Phi \, dx \Rightarrow \sum_{k=2}^{K-1} \Phi_k^* \left(\hat{H}\Phi\right)_k \Delta x + \frac{\Delta x}{2}\left[\Phi_1^* \left(\hat{H}\Phi\right)_1 + \Phi_K^* \left(\hat{H}\Phi\right)_K\right]$$

$$J = \int_0^\infty \Phi^* \Phi \, dx \Rightarrow \sum_{k=2}^{K-1} \Phi_k^* \Phi_k \Delta x + \frac{\Delta x}{2}\left[\Phi_1^* \Phi_1 + \Phi_K^* \Phi_K\right]$$

- At the endpoints, the boundary conditions give $\Phi_1 = 0$ and $\Phi_K = 0$

- **Algorithm:**

Make a guess for Φ_k and calculate $\tilde{E}$

→ Pick one Φ_k at random, e.g., Φ_l and change it by an amount randomly chosen from $(-\Delta\Phi, \Delta\Phi)$

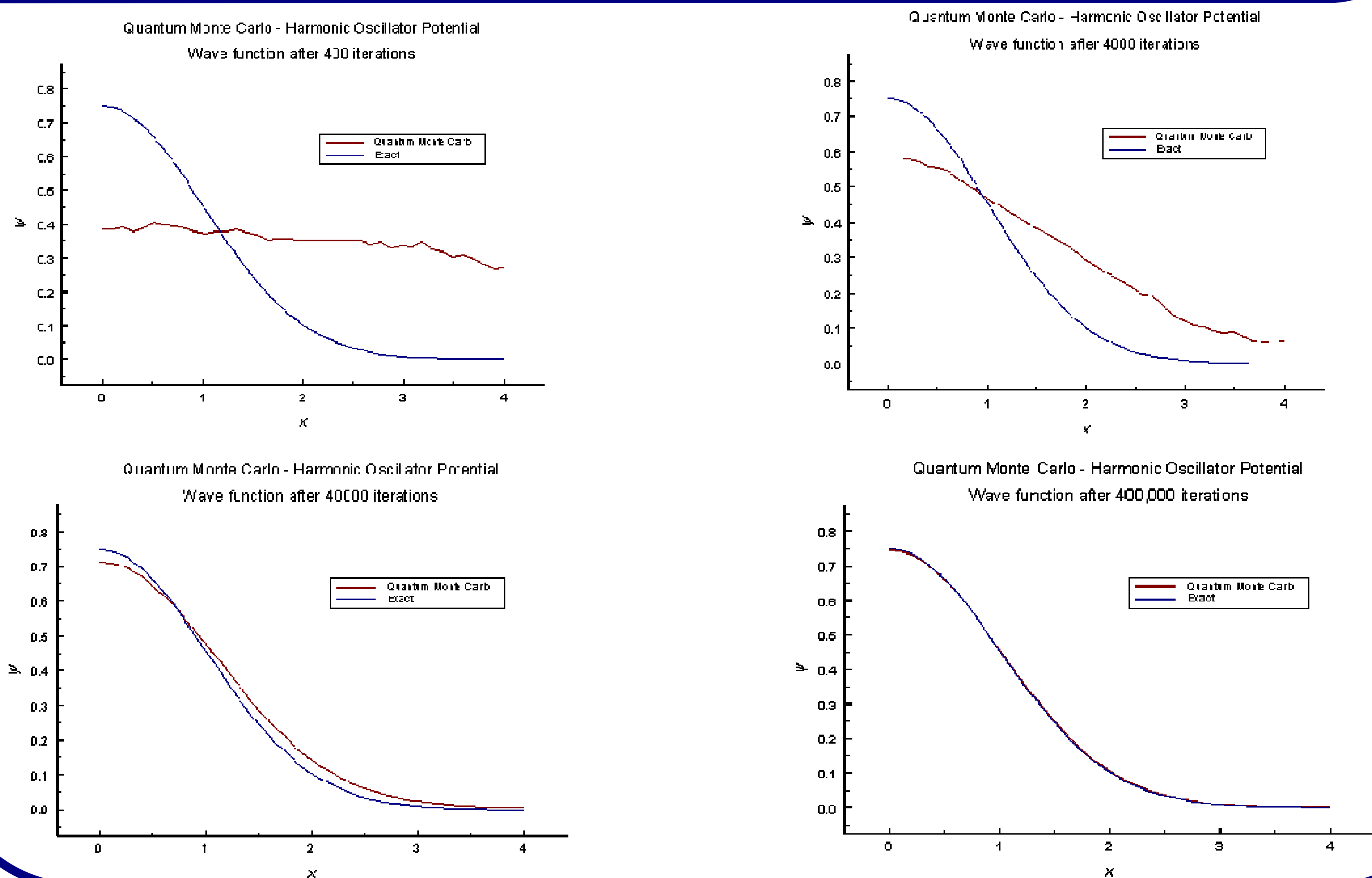
→ Recalculate $\tilde{E}$. If it is getting smaller, keep the change Φ_l in wave function value. Otherwise discard it.

→ (back to: Make a guess for Φ_k and calculate $\tilde{E}$)

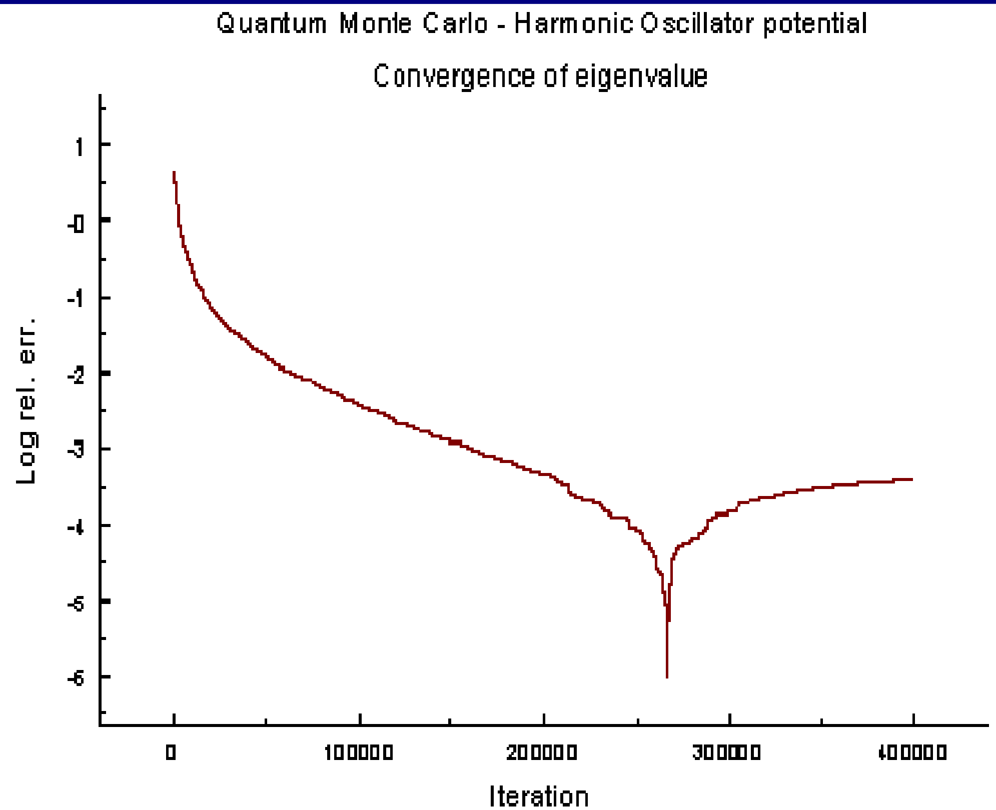
- A modification to this procedure that speeds up convergence is to make the probability that a particular grid point is chosen be proportional to $|\Phi_l|^2$, rather than uniform. The value of $\Delta\Phi$ is then chosen to be about 10% of the **mean square average** of Φ_l :

$$\Delta\Phi = 0.1\sqrt{\frac{1}{K}\sum_{k=1}^{K} \Phi_k^* \Phi_k}$$

Quantum Monte Carlo: Example $V(x) = x^2$



Quantum Monte Carlo: Rate of Convergence



- The rate of convergence of the energy eigenvalue is shown above.
- Note that the error does not go to zero. This is due to the error associated with using the **grid and the box**.