1 Plotting the H atom wavefunctions. To start, try your hand at maple. After entering maple, type x11(); if you have a screen capable of x-windows. Try plotting examples handed out in Intro to Maple. Learn more about plotting with the help commands ?plot and ?plot,options. Note in particular style, linestyle, symbol, title. [Note: you can combine several plots with different line styles and labels for each curve using with(plots): and reading the help ?plots. But this is not necessary for this example. I can live with by-hand labeling on your first curves.]

Consider a hydrogen-like atom with nuclear charge \( Z \). Make plots (a), (b) and (c) as described below. In all cases you should plot normalized wavefunctions.

a Ground state. Plot the 1s radial wavefunction for \( Z = 1, 3, 6 \). Note that you may want to make more than one plot to illustrate different features. The important feature should be highlighted in each title.

b \( n = 2 \) wavefunctions. Plot the radial wavefunctions for \( \ell = 0, 1 \). Again you should devise a way to demonstrate that the cusp conditions are satisfied.

c \( n = 3 \) wavefunctions. Plot the radial wavefunctions for \( \ell = 0, 1, 2 \). Contrast the wavefunction with the \( n = 0,1 \) cases.

2 Hydrogen atom in two and three dimensions. The aim of this problem is to understand the effect of dimensionality on the ground state of the hydrogen atom.

a Laplacians in three and two dimensions. Consider the following possible forms for the radial part of the three-dimensional and two-dimensional Laplacians.

\[
\begin{align*}
L_1 & := \text{diff}(f(r),r^2)+2*\text{diff}(f(r),r)/r : \\
L_2 & := \text{diff}(r*f(r),r^2)/r : \\
L_3 & := \text{diff}(r^2*\text{diff}(f(r),r),r)/r^2 : \\
L_4 & := \text{diff}(f(r),r^2)+\text{diff}(f(r),r)/r : \\
L_5 & := \text{diff}(r*\text{diff}(f(r),r),r)/r;
\end{align*}
\]

Discuss differences, if any, between these Laplacians. Why would one be more appropriate than another?

b For the Hamiltonian \( = \text{-Laplacian}/2 -1/r \), compute the ground state of the hydrogen atom in two and three dimensions. (Hint: try the simplest possible solution.) Comment on the difference. Work in atomic units.

c Can you explain the effect of dimensionality in increasing the bounding energy. Two possible ways are: (i) find the form of the spectrum of excited states in 2D and 3D (known); (ii) devise an appropriate variational wavefunction for studying the energy levels in a one-dimensional box (with infinite walls) as the size of the box decreases. You don’t have to do either of these suggestions. Just find a way to discuss the effect of dimensionality on the ground state.
3 Basis Functions. In solving Schrödinger equation – since an analytic solution is usually not possible – one is faced with deciding at the outset whether (a) to do a numerical solution or (b) to expand the solution in terms of basis functions and then solve a set of linear equations for the expansion coefficients. At the end of the problem explain why you think (b) is almost always chosen.

There are a number of standard basis functions that are used in quantum mechanics and solid state physics – slater orbitals, gaussian orbitals, plane waves, and shape functions. This problem explores the relative utility of the first two:

Slater orbital: \( \psi_S = \left( \frac{\eta^3}{\pi} \right)^{1/2} \exp(-\eta r) \)

Gaussian orbital: \( \psi_G = \left( \frac{2\mu}{\pi} \right)^{3/4} \exp(-\mu r^2) \)

Both of these are normalized so that \( \int d^3r \psi^2(r) = 1 \).

Use the Hamiltonian for the hydrogen atom in atomic units in the next two sections:

\[ H = -\frac{1}{2} \nabla^2 - \frac{1}{r}. \]

a Single gaussian. Determine the value of \( \eta \) and \( \mu \) that minimize the energy of the hydrogen atom for a slater and gaussian orbital wavefunction, respectively. Should the value of \( \eta \) have been expected on other grounds? Make a plot that directly compares the two normalized wavefunctions. Any comments?

b Two gaussians. Why don’t you try a better gaussian wavefunction? Consider

\[ \psi_G(r) = 0.62 \exp(-0.2r^2) + 0.86 \exp(-1.32r^2). \]

Again compute the energy with this wavefunction. Is it an improvement over the single gaussian case? Plot the wavefunction against the slater orbital found in part a. From the plot and any other inspiration, discuss how you would proceed to improve the gaussian-type wavefunction. In case you are interested some better gaussian wavefunctions for the hydrogen atom are located in [www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/gaussian.fctns.txt](http://www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/gaussian.fctns.txt)

c Discuss why analytic bases functions are preferred over numerical. And gaussian over slater.

4 Non-reflected traveling waves (solitons). While this subject has attracted a lot of high-powered mathematics (instantons, supersymmetry, etc.) none of that is needed here. In both cases the potential has been constructed to have a lowest bound state at zero energy. All wavefunctions are given; you only need to check them and to answer the questions.
a Least deep non-reflecting well. For the potential \( V_1(x) = \frac{1}{2} \left( 1 - \frac{2}{(\cosh x)^2} \right) \) show the zero-energy bound-state wavefunction is \( \frac{1}{\sqrt{2 \cosh x}} \) and the traveling wave solution is

\[
\psi_1(k, x) = \frac{-ik + \tanh x}{\sqrt{1 + k^2}} \exp(ikx).
\]

What is the energy of this state? Why is it non-reflected? Is it unique?

b Next deeper non-reflecting well. For the potential \( V_2(x) = \left( 2 - \frac{3}{(\cosh x)^2} \right) \) show the two bound states are

\[
\frac{1}{2} \sqrt{3} \frac{1}{(\cosh x)^2} \text{ and } \sqrt{3} \frac{\tanh x}{2 \cosh x}.
\]

and the traveling wave solution is

\[
\frac{(3(\tanh x)^2 - 3ik \tanh x - 1 - k^2)}{\sqrt{(4 + k^2)(1 + k^2)}} \exp(ikx).
\]

Compare the energy and group velocity of this nonreflecting state with that in part a.

c Plots. Plot the amplitude and phase of the traveling wavefunctions. Choose the value(s) of \( k \) and \( x \) to illustrate the important features. Hint: one way to do the plots in terms of an already defined wavefunction \( \text{wf}(k, x) \) is:

```maple
ptwf := proc(k,xrange)
    local wfabs, wfarg;
    with(plots):
    wfabs := plot(abs(wf(k,x)),x=-xrange..xrange,'='=0..1):
    wfarg := plot(argument(wf(k,x))/Pi,x=-xrange..xrange,'='=-1..1,
    linestyle=2):
    display({wfabs,wfarg})
end:
```

5 Compare spectra of two wells. For a three-dimensional harmonic oscillator and a spherical box, compare histogram plots of the eigenvalues of the Schrödinger equation for both problems. Set the frequency of the harmonic oscillator and spacing between the lowest two energies in the the box to be comparable. Comment on the differences in the plot. Some help may be found in [www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/sph.bessel.txt](http://www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/sph.bessel.txt) and [...]histogram.txt.

6 Harmonic oscillator: second quantization operators and coherent state. We start by stating the standard first-quantization results for the harmonics oscillator. The Hamiltonian
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is written \( H = p^2/(2m) + m\omega^2 x^2/2 \). The eigenstates, indexed by \( n \) have energy \( E_n = (n + 1/2)\hbar\omega \) and eigenfunctions

\[
\psi_n(x) = N_n e^{-\left(x^2/2x_o\right)} H_n\left(\frac{x}{\sqrt{2x_o}}\right)
\]

where the normalization \( N_n^2 = 1/(2^n n! x_o \sqrt{2\pi}) \) and \( H_n \) are the Hermite polynomials (\( H_0(z) = 1, H_1(z) = 2z, H_2(z) = 4z^2 - 2, \) etc.). The zero-point motion \( x_o \equiv \sqrt{\langle 0 | x^2 | 0 \rangle} = \sqrt{\hbar/(2m\omega)} \).

Note others define ‘\( x_o \)’ without \( 1/\sqrt{2} \) factor. (So be careful in using other sources.) Finally, if \( \Delta x \equiv \sqrt{\langle n | x^2 | n \rangle} \) and \( \Delta p \equiv \sqrt{\langle n | p^2 | n \rangle} \), then \( \Delta x\Delta p = (n + \frac{1}{2})\hbar \). If this is not familiar, please review.

**a Second quantization.** The creation and destruction operator \( a^+ \) and \( a \), respectively, are defined by

\[
a = \sqrt{\frac{m\omega}{2\hbar}} x + i \sqrt{\frac{1}{2m\omega\hbar}} p
\]

\[
a^+ = \sqrt{\frac{m\omega}{2\hbar}} x - i \sqrt{\frac{1}{2m\omega\hbar}} p.
\]

Show that (i) these operators satisfy the commutations relations \([a, a^+] = 1\), (ii) the number operator \( N \equiv a^+ a \) satisfies \( N a^+ = a^+ (N + 1) \) and hence can be interpreted as measuring the number of quantum excited, (iii) if \( |0\rangle \) denotes the ground state than the state with \( n \) quantum excited \( |n\rangle = (a^+)^n |0\rangle/\sqrt{n!} \). [Hint: it may be useful to show that \( a^+ |n\rangle = \sqrt{n+1} |n+1\rangle \) and \( a |n\rangle = \sqrt{n} |n-1\rangle \).] and (iv) the Hamiltonian can be diagonalized \( H = \hbar\omega (N + \frac{1}{2}) \).

For some operations it may be convenient to use a dimensionless form. If \( y \equiv x/x_o \), then

\[
a = \frac{1}{2} y + \frac{\partial}{\partial y} \quad \text{and} \quad a^+ = \frac{1}{2} y - \frac{\partial}{\partial y}
\]

\[
y = a + a^+ \quad \text{and} \quad \frac{\partial}{\partial y} = \frac{1}{2} (a - a^+).
\]

**b Review of time-evolution of operators.** This may be familiar to you. If not, you should make it so. Do not turn in.

Remember:

\[
O(t) = \exp(iHt/\hbar) O \exp(-iHt/\hbar) \quad \text{or} \quad \frac{dO}{dt} = \frac{i}{\hbar} [H, O(t)] \quad \text{or} \quad i\hbar \frac{dO}{dt} = [O(t), H].
\]

Show that

\[
a^+(t) = a^+(0) e^{+i\omega t}
\]

\[
a(t) = a(0) e^{-i\omega t}.
\]

**c Comparison with classical mechanics.** For the classical oscillator with motion \( x(t) = q_o \sin \omega t \) and energy \( E = \frac{1}{2} m\omega^2 q_o^2 \), compute the classical probability of the position \( W(x)_{\text{class}} \) defined as the normalized probability that the particle is at position \( x \). Convince yourself that
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\[ W(x)_{\text{class}} = \frac{2}{v(x)T} \]
where \( v(x) \) is the velocity of the particle and \( T = \frac{2\pi}{\omega} \) is the period of oscillation.

On the same plot display this classical probability and the quantum probability for an oscillator in the \( n = 16 \). Hint: what is \( q_0 \) for that state?

d  **Coherent state.** The coherent state \( |z\rangle \) is defined by

\[ |z\rangle \equiv \exp(za^+)|0\rangle, \]

where \( z \) is a complex number and \( |0\rangle \) is the ground state of the oscillator. Using \( |n\rangle = \left[ (a^+)^n/\sqrt{n!} \right]|0\rangle \) show the following:

\[ |z\rangle = \sum_{n=0}^{\infty} \frac{z^n}{\sqrt{n!}}|n\rangle \]

where \( a|z\rangle = z|z\rangle \) used below in e

\[ \langle z_1|z_2\rangle = e^{z_1\bar{z}_2} \]

\[ P_n \equiv |\langle n|z\rangle|^2/|\langle z|z\rangle| = |z|^{2n}e^{-|z|^2}/n! \text{ Poisson distribution} \]

\[ 1 = \int \frac{dz \, dz^*}{2\pi i} \langle z|e^{-z^*z}\rangle \text{ completeness} \]

\[ e^{-i\omega a^+at}|z\rangle = |ze^{-i\omega t}\rangle \equiv |z(t)\rangle \text{ time evolution}. \]

The fifth equation means the time evolution of the normalized coherent state remains a coherent state but with a new label (e.g., \( z(t) \)). Hint: if \([A, B]\) commutes with \( A \) and \( B \), then \( e^Ae^B = e^Be^Ae^{[A,B]} \). (If you did not prove this before, do it now.) This might be useful for the third item.

e  **Simple example of the use of the coherent state.** If \( \langle x|n\rangle \equiv \psi_n(x) \), then the \( x \)-representation of the normalized coherent state \( \phi_z(x) = \exp(-|z|^2/2)\langle x|z\rangle \). From the results of the part d, show

\[ \phi_z(x,t) = \exp(-|z|^2/2)\langle x|z,t\rangle, \text{ where } |z,t\rangle = \exp(-iHt/\hbar)|z\rangle \]

\[ e^{-|z|^2} \langle z(t)|x,z(t)\rangle = x_0(z(t) + z^*(t)) = 2x_0|z|\cos(\omega t - \delta) \] where \( z = |z|e^{i\delta} \)

\[ \phi_{z}(x,t) = \phi_{z}(t) e^{-i\omega t} = e^{-i\omega t} e^{z^*(t) a^+ - z(t)^* a} \psi_0(x) \]

\[ |\phi_z(x,t)|^2 = \frac{1}{\sqrt{2\pi x_0}} \exp \left[ - \frac{(x - 2x_0|z|\cos(\omega t - \delta))^2}{2x_0^2} \right]. \]

Hence a coherent state is a gaussian wave packet that does not spread out because all the terms are in phase. Finally, take the ‘classical limit’ where \( z \gg 1 \) with \( \delta = 0 \). In particular show that \( \langle \phi_z|H|\phi_z\rangle = \hbar \omega z^2 \) and that occupation number has a sharp peak at \( \bar{N} = z^2 \) and that \( (\bar{N} - \bar{N})/\bar{N} \sim 1/z \).
7 Sticking at a solid surface. This contrasts the classical behavior of a low-energy neutral atom incident on a surface (of a solid) with a weak attractive well near the surface that has a mechanism for energy loss.

For simplicity we specialize to one-dimension. The particle is an incident from the right on a potential

\[ V(x) = \begin{cases} \infty & x < 0 \\ -V_0 & 0 < x < a \\ 0 & x > a. \end{cases} \]

The inelastic mechanism will be specified separately in the classical and the quantum mechanical sections.

a Low-energy sticking of a classical particle. The inelastic mechanism is the surface itself – namely, in one-dimension we can model the solid as a set of heavy atoms connected by springs filling the line (space) \( x < 0 \). Discuss the motion of a low-energy atom from the right with energy \( E \equiv \frac{mv^2}{2} \).

What is the effect of

a.i The attractive potential in the region \( 0 < x < a \) on the particle motion?

a.ii The surface on the energy of the atom? Estimate the probability of an atom sticking on the surface as its \( E \to 0 \).

b Low energy sticking of a quantum particle with mass \( m \). Here the energy loss is via the particle scattering off the surface localized variations.

The Hamiltonian for the independent particle and the independent vibrations is

\[ H_0 = \int dx \Psi^+(x) \left( \frac{p^2}{2m} + V(x) \right) \Psi(x) + \sum_\omega \hbar \omega (a_\omega^+ a_\omega + \frac{1}{2}). \]

The vibrations are localized near the surface. To be specific, the interaction between the particle and vibrations is

\[ V_{int} = \sum_\omega \int dx \Psi^+(x) g \left( 1 - \frac{x}{a} \right) \Psi(x) (a_\omega + a_\omega^+). \]

Thus this interaction is strongest near the surface and zero at the edge of the well. There is nothing special about this form and the answer does not depend sensitively on the form. The constant \( g \) characterizes the strength of the interaction. Do the following:

b.i In what range must \( mV_0a^2/\hbar \equiv \xi^2 \) lie for there to be one bound state?

b.ii For an incident wave \( e^{-ik(x-a)} \) [the factor \( \exp(ika) \) is intended to simplify the algebra] calculate the form of (a) the wave function in the well and (b) the reflected wave for \( x > a \).
b.iii Using the golden rule, compute the scattering rate for an outgoing particle to decay into the bound state by emitting surface vibrations. Plot this scattering rate in arbitrary units as a function of $ka$ ($0 < a < 0.1$).

b.iv The probability of sticking is the transition rate divided by the incident flux of particles. How does sticking coefficient behave as $E \to 0$? Contrast this quantum mechanical result with the classical result.

8 Virial Theorem.

To start remind yourself of the time dependence of any operator $O$ under a Hamiltonian $H$.

$$O(t) = \exp(iHt/\hbar)O \exp(-iHt/\hbar) \text{ or } \frac{dO}{dt} = \frac{i}{\hbar}[H,O]$$

For any state $\psi$ that satisfies the Schrödinger equation, show that $d\langle O \rangle / dt = 0$. Note: $O(t) \equiv \langle \psi(t)|O\psi(t)\rangle$ where $|\psi(t)\rangle = \exp(-iHt/\hbar)|\psi\rangle$. Hence you can rewrite $\langle O(t) \rangle = \langle \psi|\exp(iHt/\hbar)O \exp(-iHt/\hbar)|\psi \rangle$.

a Hyperviral theorem. Let $O = \vec{r} \cdot \vec{p}$ and restrict the form of $H$ to one in which the kinetic energy $T$ depends on only the momentum operators $\vec{p}_i$ of the particles and the potential energy $V$ depends on only the distances between interacting particles (such as nuclei or electrons). But do not restrict consideration to only single-particle systems. Then show that

$$2\langle T \rangle = \langle \vec{r} \cdot \vec{\nabla}V \rangle.$$

Note this quantum mechanical virial theorem is correct only for expectations with respect to states that satisfy the Schrödinger equation.

b Harmonic oscillator. In the single-particle case, suppose that $V(r) = kr^n$. For the case of the harmonic oscillator, what relations does this yield between the expectation value of the kinetic and potential energy? Is this consistent with your earlier experience with the harmonic oscillator in classical and quantum physics?

c Coulomb Potential. For charged particles the potential has an inverse-distance relation - between electrons and nuclei it is of the form $-Ze^2/|\vec{r} - \vec{R}|$ and between two electrons of the form $e^2/|\vec{r}_i - \vec{r}_j|$. Again for an expectation value with respect to any wave function satisfying the Schrödinger equation, show

$$2\langle T \rangle = -\langle V \rangle.$$

Contrast this result with virial theorem for classical mechanics.
d Molecular Binding. A stable molecule by definition has a negative binding energy* where the binding energy is defined as the difference between ground state energy of the molecule and the sum of the ground state energies of the constituent atoms. Show this fact can be used to deduce that the change in the kinetic energy is positive while the potential energy decreases upon formation of the molecule. For the simple case of the $H_2^+$ molecular ion, show by a sketch or in some other simple way how this occurs. For the case of the $H_2$ molecule, it is possible to so simply understand that $\langle \Delta T \rangle > 0$ and $\langle \Delta V \rangle < 0$?

e Scaling and restoring the virial theorem. A standard approach to improve a variational wave function based on using atomic orbitals is to scale all the coordinates in the wavefunction by a scale factor $\eta$. A computation of the energy and minimization with respect to this value $\eta$ will always give a lower energy (provided you don’t find $\eta = 1$ is the minimum). Try this for $H_2^+$. How much improvement can you achieve? After you have done this, does the newly optimized wavefunction satisfy the virial theorem? Does that suggest that the virial theorem you have just proved is less restrictive than your proof? You may find it useful to do some analytic work, before you start doing detailed calculations. The integrals in www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/h_mol.ion.txt helpful. If you want to do one of these integral remember that $\int dx f(x)g(x) = \int (dk/2\pi)f(-k)g(k)$ and natural multi-dimensional extensions.

9 Cusp Conditions. This problem serves to illustrate the singularity forced on the wave function due to the singularity in the Coulomb potential. We include here not only the Coulomb potential felt by one electron due to the nucleus $-Z/|\vec{r}|$ but also the Coulomb potential between two electrons $i$ and $j$, $1/|\vec{r}_i - \vec{r}_j|$. As always we work in atomic units where $m_e = 1, \hbar = 1, e = 1$ and energy is measured in Hartrees (27.2 eV).

To start we observe that we can define a local energy for any exact solution of the Schrödinger equation

$$E_L = \frac{H\psi}{\psi}$$

which is finite and equal to the expectation value of the energy. This origin of this ‘miracle’ is that the contributions to the kinetic energy from particles $i$ and $j$ diverge just so to cancel the divergence in the potential energy from $1/|\vec{r}_i - \vec{r}_j|$. The contributions to the kinetic energy of the other particles is well behaved. So we can ignore all other particles and work in the system of just two particles.

There are two two-particle cases:

(A) nucleus-electron where the separation $r$ is just the electron-nucleus separation and the effective mass $\mu = 1$ (setting the nuclear mass to infinity) and

* In the literature the negativity of the binding energy is assumed, and the binding energy is usually reported as a positive number.
(B) electron-electron where the separation $r$ is just the electron-electron separation and the effective mass $\mu = 1/2$ (Why?).

a Preliminaries. Show that the condition for the local energy to be finite is

$$-\frac{\nabla^2 \psi}{2\mu \psi} + V(r) = \text{finite}.$$ 

b S-wave. When the particle(s) are in relative $s$ state, show for there to be no divergence in $E_L$ that

$$\frac{\psi'}{\psi} = \mu r V(r)$$

which corresponds to

$$\left. \frac{d \ln(\psi)}{dr} \right|_{r=0} = \begin{cases} -Z & \text{case (A)} \\ 1/2 & \text{case (B)} \end{cases}$$

c $P$-wave as an example of $l \neq 0$. In contrast to the $s$-wave case where $\psi(r = 0) \neq 0$, for $l \neq 0$, $\psi(r = 0) = 0$. (Why?) For $p$-wave, a reasonable ansatz for the wavefunction is

$$\psi \propto r \cos \theta (1 + C r)$$

and the problem is to determine $C$. To start, justify this ansatz. Then show that

$$C = \lim_{r \to 0} \frac{\mu V(r) r}{2}.$$ 

In particular, show

$$C = \begin{cases} -Z/2 & \text{case (A)} \\ 1/4 & \text{case (B)} \end{cases}$$

Note: the form of the ansatz is not unique. Another possibility is that

$$\psi \propto r \cos \theta \exp(C r).$$

Would this form change your result for $C$?

d Spin part of wave function. In the case (B) of both parts 2b and 2c, discuss the spin-part of the wave function. (Hint: this is a review of the Pauli principle.)

10 Towards the helium ground state. There is no analytic solution of the helium atom, but steadily improved variational wavefunctions have reproduced the experimental ground state (-2.904 H) and the low-lying excited states ($2^3 S$: -2.175 H, $2^3 P$: -2.133 H, $2^1 S$: -2.123 H). This exercise will explore the simplest variational wavefunctions.

This exercise has been organized to simplify the mathematics as much as possible so you may concentrate on the physics. At the end of this problem there are two appendices on
(I) integrating over interelectronic separation $|\vec{r}_1 - \vec{r}_2|$ and (II) handling the kinetic energy operator.

Finally, some possibly useful maple script for analytically performing multi-dimensional integrals is in www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/helium.ints.txt. As a rough guide the relative time for maple to analytically compute the energies for the three problems c.i/c.iii/d are in the ratio: 1/10/30.

**a** Devising a variational wavefunction. Supposing helium to have a nuclear charge of $Z$, argue that to satisfy the cusp conditions the wavefunction must be of the form

$$\exp \left[ -Z(|\vec{r}_1| + |\vec{r}_2|) + |\vec{r}_1 - \vec{r}_2|/2 \right].$$

Here $\vec{r}_i$ ($i = 1, 2$) are the vectors from the nucleus to the two electrons. Henceforth we will write the wavefunction as $\exp \left( -Z(r_1 + r_2) + r_{12}/2 \right)$.

**b** Potential and kinetic energy. Show that if trial wavefunction depends on $(r_1, r_2, r_{12})$ that the kinetic energy and potential energy can be written

$$\langle T \rangle = \left\langle \psi(r_1, r_2, r_{12}) \right\rangle^2 \left[ Z^2 + \frac{1}{4} \left( -\frac{Z^2}{r_1} + \frac{Z^2}{r_2} - \frac{r_{12}^2}{r_1 r_2} \right) + \frac{Z^2}{r_{12}^2} - \frac{r_{12}^2}{2} \right]$$

$$\langle V \rangle = \left\langle \psi(r_1, r_2, r_{12}) \right\rangle^2 \left[ -\frac{Z}{r_1} + \frac{Z}{r_2} + \frac{1}{r_{12}} \right].$$

Hint: Appendix III may be very helpful.

In the case that $\psi \propto \exp [-Z(r_1 + r_2)]$, does the kinetic energy simplify to $Z^2$?

**c** Results. For the three wavefunctions.

(i) $\exp[-Z(r_1 + r_2)]$

(ii) $\exp[-\eta(r_1 + r_2)]$ Note: you must find the $\eta$ that minimizes energy.

(iii) $\exp[-Z(r_1 + r_2) + r_{12}/2]$

Evaluate the ground state energy for $Z = 2$. Contrast these with both the Hartree-Fock result [-2.862 H] and the exact, non-relativistic, result [-2.904 H]. Do any these wavefunctions satisfy the virial theory? Can you understand how this is possible?

**d** Bonus problem. In 1930 Carl Eckart [Physical Review 36, 878] considered the following wavefunction for helium $\exp(-z_1 * r_1 - z_2 * r_2) + \exp(-z_1 * r_2 - z_2 * r_1)$. (Why this form?) Two surprises are that the minimum energy [-2.876 H] is better than Hartree-Fock and that the values of $(z_1, z_2)$ are not equal (2.183,1.189). There is a ‘saddle point’ solution at $z_1 = z_2 = 1.69$ with higher energy [-2.848 H]. The idea is that the Coulomb potential $1/r_{12}$ would be decreased if one electron was close to the nucleus ($z_1 = 2.18$) while the other was far away ($z_2 = 1.19$). The increased screening due to the closer electron allows the other electron to lie farther way. The resulting ‘in-out’ correlation leads to a deeper binding. But
even more surprising is that fact that a problem which seems completely symmetric between the two electrons has a solution that seems to break the symmetry between them.

Symmetry breaking: a solution which does not reflect the underlying symmetry of the Hamiltonian is a recurring feature of quantum mechanics. Note: in this 'baby' case, the resulting wavefunction is completely symmetric with respect to the interchange of $r_1$ and $r_2$. So the only 'symmetry breaking' in this case is that the coefficients $z_1$ and $z_2$ are different. We shall find problems where real symmetry breaking occurs.

Please try your hand at doing this calculation. For solving the resulting energy $en(z_1,z_2)$ (say), you need to use a maple script like this:

```maple
fsolve({diff(en(z1,z2),z1), diff({en(z1,z2),z2}),{z1=1..1.5,z2=2..2.5}})
```

If you don’t specify the range of the solution, you will find the one where the two exponent coefficients are equal. Try it!

**e Summary.** Make a table combining all your results including those I have told you (such as Hartree-Fock and the Eckart calculations). Comment specifically how much correlation energy is recovered by the various approximate wavefunctions.

**Appendix I.** Integrating over $r_{12}$. Use the vector identify $r_{12}^2 \equiv (\vec{r}_1 - \vec{r}_2)^2 = r_1^2 + r_2^2 - 2r_1r_2\cos\theta_{12}$. For fixed $r_1$ and $r_2$, $d\cos\theta_{12} = r_{12}dr_{12}/(r_1r_{12})$. The remaining angular integrals can be done to give

$$d^3r_1\,d^3r_2 = 8\pi^2 r_1r_2\,r_{12}dr_{12}$$

over the range

$$r_1 - r_2 < r_{12} < r_1 + r_2, \quad 0 < r_2 < r_1, \quad 0 < r_1 < \infty$$

$$r_2 - r_1 < r_{12} < r_1 + r_2, \quad 0 < r_1 < r_2, \quad 0 < r_2 < \infty.$$ 

**Appendix II.** Kinetic energy. We start with kinetic energy by integrating by parts

$$\langle T \rangle = -\frac{1}{2} \langle \psi (\nabla_\vec{r}_1^2 + \nabla_\vec{r}_2^2) \psi \rangle = \frac{1}{2} \langle \left| \nabla_\vec{r}_1 \psi \right|^2 + \left| \nabla_\vec{r}_2 \psi \right|^2 \rangle.$$

If $\psi$ is a function of $\vec{r}_1, \vec{r}_2, \vec{r}_{12} = \vec{r}_1 - \vec{r}_2$, then

$$\nabla_\vec{r}_1 = \frac{\vec{r}_1}{r_1^2} \frac{\partial}{\partial r_1} + \frac{\vec{r}_{12}}{r_{12}^2} \frac{\partial}{\partial r_{12}}$$

$$\nabla_\vec{r}_2 = \frac{\vec{r}_2}{r_2^2} \frac{\partial}{\partial r_2} + \frac{\vec{r}_{12}}{r_{12}^2} \frac{\partial}{\partial r_{12}}.$$

Noting that $2\vec{r}_1 \cdot \vec{r}_{12} = r_1^2 + r_{12}^2 - r_2^2$ and $2\vec{r}_2 \cdot \vec{r}_{12} = r_2^2 + r_{12}^2 - r_1^2$, we can write

$$\frac{1}{2} \left[ \left| \nabla_\vec{r}_1 \psi \right|^2 + \left| \nabla_\vec{r}_2 \psi \right|^2 \right] = \frac{1}{2} \left[ \left( \frac{\partial \psi}{\partial r_1} \right)^2 + \left( \frac{\partial \psi}{\partial r_2} \right)^2 \right]$$

$$+ \frac{r_1^2 + r_{12}^2 - r_2^2}{2r_1r_{12}} \frac{\partial \psi}{\partial r_1} \frac{\partial \psi}{\partial r_{12}} + \frac{r_2^2 + r_{12}^2 - r_1^2}{2r_2r_{12}} \frac{\partial \psi}{\partial r_2} \frac{\partial \psi}{\partial r_{12}}.$$
Finally we specialize to the $r_1, r_2, r_{12}$ all being positive. We make no error doing this since $(\partial/\partial x) \exp(|x|) = (\text{sgn}(x) + 2x\delta(x)) \exp(|x|)$ and the integral over the delta function yields nil.

11 Details of Hartree-Fock.

a Angular weight factors. In class we worked out the coefficients $a^2(1m_1,1m_2)$, showing they all had a common denominator of 25. This factor was used to scaled $F^2$. Prove that the denominator scale factors for the angular components are as shown in the table.

<table>
<thead>
<tr>
<th></th>
<th>$p$</th>
<th>$d$</th>
<th>$f$</th>
<th>$F^4$</th>
<th>$d$</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$</td>
<td>25</td>
<td>35</td>
<td>75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d$</td>
<td>35</td>
<td>49</td>
<td>105</td>
<td>$441$</td>
<td>693</td>
<td></td>
</tr>
<tr>
<td>$f$</td>
<td>75</td>
<td>105</td>
<td>225</td>
<td>$693$</td>
<td>$1089$</td>
<td></td>
</tr>
</tbody>
</table>

b Size of scaled $F_2$ and $F_4$. For the hydrogenic wavefunctions given below work out the sizes of $F_2(nl,n^\prime l^\prime)$ and $F_4(nl,n^\prime l^\prime)$ in cm$^{-1}$. In class we called the scaled $F$’s by $\tilde{F}$. Here we use the symbols $F_2$ and $F_4$ for $F^2$ and $F^4$ scaled by the denominator factors in section a. (Hint: $F_2(3d,3d) = 203Z$ and $F_4(3d,3d) = 14.7Z$.) The actual values are something like a factor of two larger; so these estimates are useful. Do cases for only $l = 1, 2, 3$.

\[
\begin{align*}
R_{1s}(r) &= 2Z^{3/2}r e^{-Zr} \\
R_{2s}(r) &= \frac{1}{\sqrt{2}}Z^{3/2}r e^{-\frac{Zr}{4}} \left(1 - \frac{Zr}{2}\right) \\
R_{3s}(r) &= \frac{2}{3\sqrt{3}}Z^{3/2}r e^{-\frac{Zr}{4}} \left(1 - \frac{2Zr}{3} + \frac{2Z^2r^2}{27}\right) \\
R_{4s}(r) &= \frac{1}{4}Z^{3/2}r e^{-\frac{Zr}{4}} \left(1 - \frac{3Zr}{4} + \frac{Z^2r^2}{8} - \frac{Z^3r^3}{192}\right) \\
R_{2p}(r) &= \frac{1}{2\sqrt{6}}Z^{5/2}r^2 e^{-\frac{Zr}{2}} \\
R_{3p}(r) &= \frac{8}{27\sqrt{6}}Z^{5/2}r^2 e^{-\frac{Zr}{3}} \left(1 - \frac{Zr}{6}\right) \\
R_{4p}(r) &= \frac{\sqrt{15}}{48}Z^{5/2}r^2 e^{-\frac{Zr}{4}} \left(1 - \frac{Zr}{4} + \frac{Z^2r^2}{80}\right) \\
R_{3d}(r) &= \frac{4}{81\sqrt{30}}Z^{7/2}r^3 e^{-\frac{Zr}{3}} \\
R_{4d}(r) &= \frac{1}{64\sqrt{5}}Z^{7/2}r^3 e^{-\frac{Zr}{4}} \left(1 - \frac{Zr}{12}\right) \\
R_{4f}(r) &= \frac{1}{768\sqrt{35}}Z^{9/2}r^4 e^{-\frac{Zr}{4}}
\end{align*}
\]

A useful maple script may be found in [wilkins.maple.handouts]f2and4.ints.

c Comparing $d^2$ and $dd$. The three lowest $d^2$ terms are $E^{(3)F} = F_0 - 8F_2 - 9F_4$, $E^{(1)D} = F_0 - 3F_2 + 36F_4$ and $E^{(3)P} = F_0 + 7F_2 - 84F_4$. Compare estimated with experimental (in
parentheses) splittings in cm\(^{-1}\) for Ti\(^{+2}\) \((D - F: 8200, P - F: 10400)\) and for Ni\(^{+8}\) \((D - F: 22000, P - F: 25000)\). For the case of Sc\(^{+}\) excited to the 3d4d configuration \((D - F: 650, P - F: 1020)\), explain what contributions are missing from the formulas above. Hint: what value of \(Z\) should you use in each case?

12 Hartree-Fock Treatement of Free Electron Gas. The term ‘free electron’ refers to the single-particle Hamiltonian being \(\int d^3\vec{x} \psi^+(\vec{x})\vec{p}^2/(2m)\psi(\vec{x})\) which has plane-wave solutions \(\psi_k(x) = \exp(i\vec{k} \cdot \vec{x})/\sqrt{V}\) and single-particle energies \(\epsilon_k = (\hbar k)^2/(2m)\).

In this problem we work at zero temperature. For that case all \(k\) states are filled up to the Fermi wave vector \(k_F\). If we set the volume \(V = 1\) the density of electrons is equal to the number of electrons of both spins \(N = k_F^3/(3\pi^2)\). Another important quantity is the free-electron Fermi energy \(E_{F}^{(0)} = (\hbar k_F)^2/(2m)\).

A common way of characterizing the density of the electron gas is in terms of the radius \(r_s\) (measured in unit of the Bohr radius \(a_o\)) of a sphere that contains one electron. Show that \(r_s a_o k_F = (4\pi/3)^{1/3} = 1.919\). For most metals, \(2 < r_s < 6\).

a Energy. Prove that the plane waves \(\psi_k(\vec{x})\) are solutions of the Hartree-Fock equations and that the single-particle energy can be written in terms of a self-energy \(V_F(k)\):

\[
E_k = \epsilon_k + V_F(k)
\]

\[
V_F(k) = -\frac{e^2 k_F}{\pi} \left[ 1 + \frac{k^2 - k_F^2}{2kk_F} \ln \left| \frac{k - k_F}{k + k_F} \right| \right].
\]

On the same plot display \(\epsilon_k\) and \(E_k\) in the range \(0 < k < 2k_F\) for the case \(r_s = 3.015\) (not an innocent choice).

Finally work out the total energy of the electron gas per particle \((E_{HF}/N)\) and show it can be written

\[
\frac{E_{HF}}{N} = 1.105 \frac{r_s^2}{r_s} - 0.458 \frac{r_s}{H(\text{artrees})}.
\]

Find the value of \(r_s\) which minimizes this energy. Comment why metals can be stable for a range of \(r_s\).

b Specific Heat. From a course in statistical mechanics you could have learned (but probably didn’t) the following formula for the specific heat of a fermions system:

\[
C = k_B T \frac{1}{V} \int d\xi N(\xi) \left( \frac{\xi}{k_B T} \right)^2 \partial f(\xi/(k_B T)) / \partial(\xi/(k_B T)).
\]

Since the Fermi function is a function of \(\xi/(k_B T)\) every ‘power’ of \(\xi\) will produce one ‘power’ of \(T\) in the specific heat. In the formula above if \(N(\xi)\) is constant for small \(\xi\) then the specific heat is linear in \(T\).
In this formula energies are measured from the interacting Fermi energy

\[ \xi = E_k - E_{k_F} \]

Note: not \( E_k - E_F^{(0)} \).

The density of state \( N(\xi) \) is proportional to \( d\xi/dE_k \) or, more precisely,

\[ N(\xi) \propto \frac{1}{d\xi/dk} \bigg|_{\xi=E_k-E_{k_F}=\frac{dE_k}{dk}(k-k_F)} \].

Using the single-particle energy deduced in part a show the specific heat at very low temperatures \( k_B T \ll E_F^{(0)} \) is proportional to \( T/\ln T \)? What do you think this 1936 result of Bardeen did for the standing of HF theory of metals? (Indeed, such a mean field approach did not begin to recover until after Landau’s Fermi Liquid Theory in the 1950’s.

c Correlation Hole. The structure (or form) factor \( S(r) \) is actually a density-density correlation function.

\[
S(\vec{r}) = \frac{1}{N} \langle 0 | \int d^3r' \rho(\vec{r} + \vec{r}')\rho(\vec{r}') | 0 \rangle
\]

\[
= \frac{1}{N} \langle 0 | \int d^3r' \sum_{i}^{N} \delta(\vec{r} + \vec{r}' - \vec{r}_i) \sum_{j}^{N} \delta(\vec{r}' - \vec{r}_j) | 0 \rangle
\]

\[
= \delta(\vec{r}) + \langle 0 | \sum_{i \neq j} \delta(\vec{r} + \vec{r}_j - \vec{r}_i) | 0 \rangle
\]

\[
\equiv \delta(\vec{r}) + (N-1)g(\vec{r}).
\]

Here \( g(\vec{r}) \) is the called the pair-distribution function. We will calculate it for the case the ground state wavefunction \( |0\rangle \) is the Hartree-Fock state for the free-electron gas.

It turns out to be easier to do this in momentum space. Show that Fourier transform of the structure factor \( S(\vec{q}) \) (the name is usually reserved for the momentum-space version) can be rewritten thusly.

\[
S(\vec{q}) = 1 + (N-1)g(\vec{q})
\]

\[
= \frac{1}{N} \langle \rho_{\vec{q}p} \rho_{-\vec{q}} \rangle
\]

\[
= \frac{1}{N} \sum_{ps} \sum_{p' s'} \langle c_{p+q,s}^+ c_{p,s} c_{p'+q',s'} c_{p'+q',s'} \rangle
\]

\[
= N\delta_{q,0} + \frac{1}{N} \sum_{p,q,s \neq 0} n_{p+q,s} (1 - n_{ps}).
\]

Finally show that

\[
S(q) = \begin{cases} 
N\delta_{q,0} + \frac{3}{2} \frac{q}{2k_F} - \frac{1}{2} \left( \frac{q}{2k_F} \right)^2, & q < 2k_F \\
1, & q > 2k_F
\end{cases}
\]
Hint: the last result can be easily deduced by drawing a good picture and seeing that $NS(q)$ is the intersection of the inside of one sphere (of radius $k_F$) and the outside of another sphere (also of radius $k_F$) displaced from the first by $\vec{q}$. This volume can easily be calculated as the volume of one full sphere minus twice the volume under a cap defined by the circle formed by the intersection of the two spheres.

By taking a Fourier transform show that the pair correlation function in the Hartree-Fock approximation is (replacing $N - 1$ by $N$)

$$ g_{HF}(r) = 1 - \frac{1}{N-1} \sum_{q<2k_F} e^{i\vec{q} \cdot \vec{r}} \left[ 1 - \frac{3}{2} \frac{q}{2k_F} + \frac{1}{2} \left( \frac{q}{2k_F} \right)^2 \right] $$

$$ = 1 - \frac{9}{2} \left( \frac{\sin(k_F r) - k_F r \cos(k_F r)}{(k_F r)^3} \right)^2. $$

Plot $g_{HF}(r)$ and compute the volume of $\int d^3r [1 - g_{HF}(r)]$. Interpret this result $(1/N)$ in terms of the discussion in class.

13 Correlation energy of the two-site Hubbard model. The Hubbard model for two sites (e.g., a molecule) depends on the site energy $\epsilon$, the hopping matrix element between the two sites $t$, and the Coulomb repulsion when both spins on a single sites are occupied $U$:

$$ H = \epsilon \sum_{i=1,2,s=\uparrow,\downarrow} c^+_{is} c_{is} + t \sum_{s=\uparrow,\downarrow} \left( c^+_{1s} c_{2s} + c^+_{2s} c_{1s} \right) + U \sum_{i=1,2} n_{i\uparrow} n_{i\downarrow}. $$

a Hartree-Fock solution. Using the method in class or some other method derive the Hartree-Fock equations for the Hamiltonian above. In particular, show the self-consistent Hamiltonian is

$$ H_{SCF} = \sum_{i=1,2,s=\uparrow,\downarrow} (\epsilon + U \langle n_{i-s} \rangle) n_{is} + t \sum_{s=\uparrow,\downarrow} \left( c^+_{1s} c_{2s} + c^+_{2s} c_{1s} \right). $$

What is the expression for the total energy?

For the case of two electrons on the molecule, solve the Hartree-Fock equations and find the ground state Hartree-Fock energy

$$ E_{HF} = 2(\epsilon - |t|) + \frac{U}{2}. $$

Did you need to assume any symmetries? Do you believe that any asymmetric solution of the HF equations could ever have lower energy?

b Exact states of Hubbard Hamiltonian. Consider all the possible states for a total occupancy $N$. Convince yourself that you need consider only “charge sectors” $N = 2$ and $N = 3$. Find
the ground states for each charge sector. Which of these sectors has the lowest energy? You may assume \( \epsilon \ll U, |t| \) for this last question. Use this lowest energy charge sector in the next part.

c Correlation energy. Find a formula for the correlation energy. Evaluate it to leading order in \( U/t \) and separately to leading order in \( t/U \). Can you understand either limiting case?

14 Correlation energy of \( \text{H}_2 \) with a minimal basis. In our initial treatment of \( \text{H}_2 \) in class, we considered two orbitals \( \psi_1 \) – a bonding orbital with even (gerade) symmetry – and \( \psi_2 \) – a anti-bonding orbital with odd (ungerade) symmetry. We shall use this minimal basis to do a full configuration interaction (CI) calculation for \( \text{H}_2 \).

The Hartree-Fock ground state wavefunction can be written

\[
|\text{HF}\rangle = |\psi_1 \psi_1\rangle \equiv |11\rangle
\]

where the notation (note overline implies down-spin )

\[
|r\bar{s}\rangle = \begin{vmatrix}
\psi_\alpha(1) \\
\psi_\alpha(2)
\end{vmatrix}
\begin{vmatrix}
\psi_\beta(1) \\
\psi_\beta(2)
\end{vmatrix}
\]

Some other notational ‘advances’ are:

\[
h_i = \langle \Psi_i | \text{all single-particle operators} | \Psi_i \rangle
\]

\[
J_{ij} = V_{ij,ij} \quad \text{(Direct or Hartree term)}
\]

\[
K_{ij} = V_{ij,ji} \quad \text{(Fock term)}
\]

\[= V_{ii,jj} \quad \text{if wavefunctions are real.}\]

a CI matrix in this minimal basis. While the full CI expansion might appear to be

\[
|\text{CI}\rangle = c_0|\text{HF}\rangle + c_1 \frac{1}{\sqrt{2}} \left( |1\bar{2}\rangle + |2\bar{1}\rangle \right) + c_2 |22\rangle,
\]

show that the \( c_1 \) term can be omitted since it is odd under inversion through the center of molecule. Show then that the CI matrix reduces to

\[
H = \begin{pmatrix}
2h_1 + J_{11} & K_{12} \\
K_{12} & 2h_2 + J_{22}
\end{pmatrix}
\]

We can work in terms of the HF orbital energies: \( \epsilon_1 = h_1 + J_{11} \) and \( \epsilon_2 = h_2 + 2J_{12} - K_{12} \), where \( \epsilon_2 \) is the energy of an extra electron in \( \psi_2 \) orbital. Rewrite the CI matrix eliminating the single-body terms \( h_1 \) and \( h_2 \).

b Correlation energy. In terms of the

\[
2\Delta \equiv \langle 22|H - E_{\text{HF}}|2\bar{2}\rangle = 2(\epsilon_2 - \epsilon_1) + J_{11} + J_{22} - 4J_{12} + 2K_{12},
\]

16
Show the correlation energy

\[ E_{\text{corr}} = \Delta - \sqrt{\Delta^2 + K_{12}^2} \]

By expanding this result in some defendable way, show that the correlation energy reduces to the estimate made in class:

\[ E_{\text{corr}} \approx -\frac{\langle 22|H|HF\rangle^2}{\langle 22|H - E_HF|22\rangle} \]

15 Quantum Collapse and Revival of Rabi Oscillations.

This problem is concerned with an atomic two-level system that is interacting with a resonant laser field. We start with making reasonable approximations and simplifications in order to derive the solution for a quantized light field with a single occupied mode. We then introduce a coherent-state description of the light field, and discover some interesting quantum phenomena.

a The Hamiltonian. The Hamiltonian for a one-electron atom in a vector potential \( \mathbf{A} \) is:

\[ H = \left( \frac{p - e\mathbf{A}/c}{2m} \right)^2 + V(r) + H_{\text{field}} \]

where \( V \) is the atomic potential and \( H_{\text{field}} \) is the Hamiltonian of the electromagnetic field.

The system we shall study – the Jaynes–Cummings model – consists of two atomic levels, with energy \( E_1 \) and \( E_0 \), of different parity interacting with a vector potential of a single quantized mode:

\[ \mathbf{A}(r) = u(r)(a^\dagger + a), \]

where \( a \) is the annihilation operator for the mode. We assume that the mode function, \( u(r) \), is real for simplicity (the normalization factors are included in the mode function). In the dipole approximation the mode function is assumed constant over the atom. Show that we can then derive a simplified Hamiltonian, (interaction linear in \( \mathbf{A} \)) of the form:

\[ H = H_{\text{atom}} + H_{\text{field}} + H_{\text{int}} = \sum_{i=0,1} E_i c_i^\dagger c_i + \hbar \omega a^\dagger a + \left( dc_i^\dagger c_0 + d^* c_0^\dagger c_1 \right) (a^\dagger + a) \]

where \( d = e u(\mathbf{r}_{\text{atom}}) \cdot \mathbf{p}_{10}/mc \), and \( c_i \) is the destruction operator for the electron state \( i \).

b The eigenstates. First we shall make a transformation to the interaction picture, that is, make the transformation

\[ H_{\text{int}}(t) = \exp(iH_0 t/\hbar)H_{\text{int}}\exp(-iH_0 t/\hbar), \]

where in our case \( H_0 = H_{\text{atom}} + H_{\text{field}} \). When you make this transformation for the resonant case, \( E_1 - E_0 = \hbar \omega \), you
will find some constant terms and some that oscillate with frequency $2\omega$. In the so-called ‘resonant approximation’ (or rotating-wave approximation) these rapidly oscillating terms are neglected. Show that we then get a constant interaction term:

$$H_{\text{int}}(t) = dc_1\dagger c_0 a + d^* c_0\dagger c_1 a\dagger$$

Hence, for a mode with $n$ quanta when the atom is in the lower state we need to consider only the states $|0; n\rangle$ and $|1; n-1\rangle$. Diagonalize the Hamiltonian and show that the eigenstates are $(|0; n\rangle \pm |1; n-1\rangle)/\sqrt{2}$, with energies $\pm|d|\sqrt{n}$.

c **Rabi oscillations.** Show that if at $t=0$ the system is in the state $|0; n\rangle$, the probability of finding the atom in state 0 at time $t$ is

$$P_0 = \cos^2 \Omega_n t = \frac{1}{2} + \frac{1}{2} \cos 2\Omega_n t$$

where $\Omega_n = |d|\sqrt{n}/\hbar$.

The population of the atomic level is therefore an oscillatory function of time. These oscillations are typical for resonant systems and are called Rabi oscillations, after I. I. Rabi, who investigated this phenomenon in magnetic resonances experiments (1937).

d **Collapse and revival.** Consider what happens when the laser mode is in a coherent state with a distribution $P_n = \bar{n}^n \exp(-\bar{n})/n!$ for $n$ quanta. For large enough $\bar{n}$, $P_n$ is an approximately symmetric distribution peaked around a value $\bar{n}$ and with width $\sqrt{\bar{n}}$.

The probability of finding the atom in state 0 is now a statistical sum over the single mode result:

$$P_0 = \frac{1}{2} + \frac{1}{2} \sum_n P_n \cos 2\Omega_n t.$$ 

Use the general properties of the discrete Fourier transform and the assumptions above about $P_n$ to show that $P_0$ will perform Rabi oscillations of the center frequency, $\Omega_{\bar{n}}$, but decay over a time of order $\hbar/|d|$ (the collapse), but then reappear after a time $2\pi\hbar\sqrt{\bar{n}}/|d|$ (the revival).

In particular make a plot for $P_0$ to illustrate these general results. A sample maple script is attached. it can also be found in [www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/rabi.plts.txt](http://www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/rabi.plts.txt).

e **Experiment.** The figures show the first verification of the collapse and revival of Rabi oscillations [G. Rempe et al., Phys. Rev. Lett. 58, 353 (1987)]. Fig. 1 illustrates the experimental set-up: An atomic beam of rubidium atoms pass through a velocity selector and are excited by a laser to a state selected for strong Rabi coupling (specifically, the Rb 63p Rydberg state). The atoms (now with a known state and velocity) then pass through the microwave cavity, in which a single mode is excited. The mode frequency is resonant with a transition to a lower state (the 61d state in Rb), which situation corresponds to our model. Lastly, the
atoms that have passed through the cavity are investigated, and the number of atoms still in
the upper state is determined (by registering the change in field ionization with and without
the cavity active). Note that the time that the atom spends in the cavity is given by the
known velocity, so that by varying the velocity the population at different interaction times
can be measured.

To apply our results we need to know the average number of photons in the cavity. This is not
that easy to determine, and we will just quote the result, which is quite simple: \( \bar{n} = T_c N / 2 \)
where \( T_c \) is the characteristic decay time of the cavity and \( N \) is the flux of atoms in the
Rydberg state.

Figures 3–5 show the results of the experiments. Use Fig. 3 to obtain an approximate value
for the parameter \(|d|\) and use this result to verify that the time scales for the collapse in Fig.
4 and the revival in Fig. 5 are consistent with our results. In all three cases \( T_c = 2 \) ms, while
the flux, \( N \), equals 500, 2000, and 3000 s\(^{-1}\), respectively. (The average number of photons is
quite small, so our assumptions about the distribution is not really applicable, but we can
still use the formulas to see if the orders of magnitude are right.)

\[
ff := \text{proc}(na,d,lower,upper,max) \quad \text{local freq, step, size, summax, p, pt, n, j, tmp; } \\
global aa; \\
p := \text{proc}(n,na) \text{ na}^n \text{exp(-na)/n! end}; \\
freq := d*sqrt(na); \\
step := 0.1/freq; \\
size := round(1+(upper-lower)/step); \\
summax := round(max*na); \\
aa := \text{array}(1..2*size); \\
for j to size do \\
    aa[2*j-1] := step*(j-1); \\
tmp := 1/2; \\
for n from 0 to summax do \\
    tmp := tmp + evalf( \\
       1/2+1/2*p(n,na)*cos(2*d*sqrt(n)*step*j)) \\
    od; \\
aa[2*j] := tmp; \\
om
16 Diffusion Quantum Monte Carlo Approach. For many-body systems a central technical difficulty is that number of configurations goes exponentially. Consider a lattice which at each site has four possible levels. Then for a lattice with \( N \) sites, the number of configurations grows as \( 4^N \). Clearly statistical methods which effectively sample the most important of these configurations could be a help. One of these statistical methods, Diffusion Monte Carlo, is illustrated here for a sufficiently simple problem that all approximations can be checked against the exact energy and wave function.

The diffusion Monte Carlo method is based on the evolution of the state under repeated applications of the Hamiltonian \( H \). In particular, for any state \( \phi \) that has non-zero-overlap with the ground state \( \phi_o \), \( \lim_{t \to \infty} \exp(-Ht)\phi = \phi_o \). Note that we have rotated the time to the negative imaginary axis \( (t \to -it) \) so that an oscillating time dependence becomes a convergent one: \( \exp(iHt) \to \exp(-Ht) \).

The wave function evolves in space via a green function, again for time running along the negative imaginary axis:

\[
\psi(x, t + \tau) = \int_{-\infty}^{\infty} dx' g(x, x', \tau) \psi(x', t) \tag{1}
\]

where the green function \( g(x, x', \tau) \) is defined by

\[
\left( H + \frac{\partial}{\partial \tau} \right) g(x, x', \tau) = \delta(x - x')
\]

\[
\int_{-\infty}^{\infty} dx' g(x, x', \tau) = 1.
\]

In this problem we compute the ground state in box of length 2 \((-1 \leq x \leq 1)\). For a constant potential \( H = -(1/2)\frac{d^2}{dx^2} \), the green function \( (g \equiv \exp(-H\tau)) \) has the simple form

\[
g(x, x', \tau) = \exp \left( -\frac{1}{2} \left( \frac{x - x'}{\sqrt{\tau}} \right)^2 \right) \sqrt{2\pi\tau} \tag{2}
\]

There are two important points. First, in a finite box we must correct the green function to make sure it goes to zero at the edge of the box. In the limit of short time \( (\tau) \), we can approximate it by

\[
\begin{cases} 
  g(x, x', \tau) - g(x, Ix', \tau) & \text{if } x \text{ and } x' \text{ inside box} \\
  0, & \text{otherwise}
\end{cases}
\]

* Imagine in this discussion the ground state energy \( E_o \) is subtracted from the Hamiltonian.
Here $Ix'$ denotes the mirror image of $x'$ with respect to the closer side of the box. In the equation (1) we include this effect by multiplying $g(x,x',\tau)$ by $K(x,x',\tau)$ (say)

$$K(x,x',\tau) = \begin{cases} 1 - \frac{g(x,Ix',\tau)}{g(x,x',\tau)} \equiv 1 - P(x,x',\tau), & \text{if } x, x' \text{ in the box} \\ 0, & \text{otherwise.} \end{cases}$$

For $x'$ near the right side of the box

$$P(x,x',\tau) = \left(-\frac{[(x-x')^2 - (x-2+x')^2]}{2\tau}\right) = \exp\left(-\frac{2(1-x)(1-x')}{\tau}\right).$$

We view $K(x,x',\tau)$ as a probability with which to accept the new position $x'$. In the code we do this by accepting $x$ if $P(x,x',\tau)$ is less than a random number.

**Second,** we do not integrate Equation (1); instead we sample it. Note the variable $(x-x')/\sqrt{\tau}$ in (2) has a gaussian distribution with unit variance. Accordingly, we estimate the distance between a new position $x$ and a previous one $x'$ by $\sqrt{\tau}$ time a random number from this gaussian distribution. Clearly this procedure improves as $\tau$ decreases.

In the case where the Hamiltonian is more complicated than this here (for example, having a potential $V(x)$ depending on position), we would have to invent a more detailed way of sampling the green function. This is generally done using importance sample which is not discussed here. This tends to slow any code down. Indeed much labor goes into improving the sampling of the green function.

**Walkers.** The central idea of Diffusion Monte Carlo is that we replace the actual wave functions with a distribution of positions whose distribution is that of the wave function. In other words, we interpret the wave function as a probability which can be represented by the distribution of positions. Hence Equation (1) now generates a new position (walker) from a previous position. The accuracy of the method depends on the number of the walkers and how well their distribution represents the ground state. The longer we evolve the walkers via (1) the better the wave function.

The number of walkers is kept fixed in the routine supplied you. Hence the accuracy depends on the number of walkers, but the running time scales with the number of walkers. In better programs the number of walkers is allowed to vary. Doing so would raise several technical issues which might cloud the basic scheme being described.

The calculation of the energy is trickier. It depends on a trial wave function $\phi_T$ which is has the gross features of the actual wave function. The better the trial wave function the better the energy. If $\{x_i\}$ is the distribution of ground state walkers, mimicking the exact wave function, then

$$E = \frac{\sum_{\{x_i\}} H\phi_T(x_i)}{\sum_{\{x_i\}} \phi_T(x_i)}. \quad (3)$$
In the code supplied you, the unrenormalized \( \phi_T(x) = (1 - x^2)^2 \).

Finally here is the plan of the code (see www.physics.ohio-state.edu/~wilkins/quantum/Maplescripts/diffusion.mc.txt):

- Initialize walkers [selecting random numbers between -1 and 1.]
- Equilibrate walkers by sweeping through all the walkers a number of times.
- Make a measurement of the energy. This has two parts.
  - Within an block, do a number of sweeps through all the walkers to compute an energy.
  - Repeat for a sufficient number of block to reduce (and estimate) the statistical error in the measurement.
- Report the energy and the estimate of its error.
- Make a histogram of the walker distribution generated during the measurement cycle.

**a** Dependence on parameters. How does the statistical error depend on the number of walkers? How does the statistical error depend on the number of measurement blocks? If number of sweeps in block is reduced to a small number is the answer affected? (Hint: what is required so that measurement of the energy in a block is statistically independent of the measurement in an adjacent block? If the measurement are not statistically independent will this also affect our estimate of the statistical error?)

**b** Dependence on trial wave function. If \( \phi_T \) is the exact ground state wave function, how does the Monte Carlo estimate of the energy change? Invent a better trial wave function that has a better variational energy than the current trial wave function and modify the routine energy to use it. Does the use of a better trial wave function affect the energy estimate and/or the statistical error?

**c** Energy as function of the time \( \tau \). Before you try an computation, consider an initial uniform wave function which can be expanded in terms of the eigenfunctions inside the box. How will successive applications of \( \exp(-H\tau) \) affect the expansion. (Hint: you may find it simpler to use \( H - E_o \).) Predict how long it will take the energy to converge. Now modify the program to make a measurement every step and check this prediction. You will need to use a large number of walkers (\( \sim 10^3 \)). So think a lot about the calculation before you modify the program. Otherwise you will spend all your time waiting for useless results.

**d** Option: Going beyond the box. Think about how you would proceed in one of the following cases: (a) one particle in a non-uniform potential \( V(x) \); (b) More than one particle with some interaction between them. While you could use importance sampling (whatever that is), try to consider how to proceed using only what you have learned so far and your knowledge of quantum mechanics. See the next two paragraphs for some help in thinking about these possibilities.

Suppose we introduce an extra non-uniform potential inside the box. That is, \( \hat{H} = H + V(x) \), where \( H \) is the current particle-in-a-box Hamiltonian and \( V(x) \) is 1 if \( 0 \leq x \leq 0.5 \) and 0 otherwise.
The green function for $\tilde{H}$ is defined as $\exp(-\tilde{H}\tau)$. To order $\tau^2$, this can be written as $g(x, x', \tau)\exp(-\tau V(x'))$, where $g(x, x', \tau)$ is the current green function, i.e., that of $H$. Therefore in carrying out Eq. (1) for the new problem, we need to insert an extra factor $W(x') \equiv \exp(-\tau V(x'))$ between $g$ and $\psi$ on the right-hand side. Note that $0 \leq W(x') \leq 1$ and can thus be viewed as a probability. Now recall the three steps involved in generating a new walker: (a) randomly select a walker $x'$; (b) sample a new position $x$ from Eq. (2); (c) accept $x$ with probability $K(x, x', \tau)$. To account for $W(x')$, we can add, between steps (a) and (b), a step (a') in which we accept the selected walker $x'$ with probability $W(x')$. In other words, we draw a random number; if it is less than $W(x')$, we proceed to step (b); otherwise we return to step (a).

Consider now $N$ interacting distinguishable particles. The advantage of Monte Carlo approaches is enhanced as the dimensionality of the Hilbert space grows. Let $x \equiv \{r_1, r_2, \ldots, r_N\}$, where $r_i$ denotes the position of the $i$-th particle. Now each walker is an $N$-dimensional vector consisting of a configuration of the $N$ particles, i.e., it gives a “snapshot” of the system, but the formalism we have established for one particle remains valid and in principle carries through. Particle interaction can be handled the same way as $V(x)$ in the above paragraph, since it is a number that can be computed for any given configuration $x$. 