Recommended practice (answers given):

#1 on 2011 final
#1 on 2009 midterm
#1 on 2007 midterm
#3 and #4 on 2010 midterm
#2 and #3 on 2011 midterm

1) In the theory of enzyme kinetics a popular model that says the barrier crossing dynamics involve a "rate promoting coordinate" \( Q(t) \) whose dynamics follow the differential equation:

\[
Q''(t) = -\omega_Q^2 Q(t) - \frac{c}{m_Q} (s(t)^2 - s_0^2)
\]

All parameters are constants except for \( s(t) \), a terribly complicated function that we cannot possibly write in closed form. Nevertheless, show that the formal solution for \( Q(t) \) is

\[
Q(t) = Q_H(t) + Q_P(t)
\]

where

\[
Q_H(t) = Q_0 \cos(\omega_Q t) + \frac{V_0}{\omega_Q} \sin(\omega_Q t)
\]

and

\[
Q_P(t) = -\frac{c}{m_Q \omega_Q^2} (s^2(t) - s_0^2) + \frac{c}{m_Q \omega_Q} \int_0^t \cos(\omega_Q (t - \tau)) 2s(\tau)s'(\tau) d\tau
\]

After you have verified the solution, show how you could obtain it by variation of parameters.

2) Consider a polymerization reaction with a mechanism

\[
M_1 \xrightarrow{k_i} P_1 \quad \text{(initiation)}
\]

\[
P_j + M_1 \xrightarrow{k_p} P_{j+1} \quad \text{(propagation)}
\]

\[
P_j + M_1 \xrightarrow{k_T} M_{j+1} \quad \text{(termination)}
\]

Where \( P_j \) refers to an actively polymerizing \( j \)-mer, \( M_1 \) refers to a monomer, and \( M_j \) refers to a capped (extinct) \( j \)-mer. Let \( M \) and \( P \) also refer to the populations of these species. Let the initial conditions be \( P_j(t) = 0 \) for \( j = 1, 2, 3, \ldots \)

A. Give an ODE in time \( t \) for \( P_1(t) \). Use the change of variables
\[ \tau = \int_0^t M_i(s)ds \]

and \( P_1(0) = 0 \) to show that

\[ P_1(\tau) = \frac{k_i}{k_p + k_i} \left( 1 - \exp[-(k_p + k_i)\tau] \right) \]

B. Now suppose that the extent of polymerization \((j)\) can become very large and that any given time the population of polymers of similar lengths are comparable, i.e. \( P(j+1, t) \) is comparable to \( P(j, t) \). If we think of \( j \) as a continuous variable then in the infinite system of ODEs, each term \( k_p P_{j-1} M_1 - k_p P_j M_1 \approx -k_p M_1 \partial P_j / \partial j \). The system of ODEs then becomes a PDE

\[ \frac{1}{M_1(t)} \frac{\partial P}{\partial t} + k_p \frac{\partial P}{\partial j} = -k_i P \]

With the change of variables above this becomes

\[ \frac{\partial P}{\partial \tau} + k_p \frac{\partial P}{\partial j} = -k_i P \]

Solve the PDE. Note that you can interpret \( P(j, 0) = 0 \) as an initial condition in \( \tau \), but you could also interpret \( P_1(\tau) \) as an initial condition in \( j \). Hint: the solution will be zero for \( j > 1 + k_p \tau \).

3) Linear Stability Analysis

The Belusov-Zhabotinsky reaction involves components \( X, Y, \) and \( Z \) in solution. Using \( X, Y, Z \) for the concentrations of the reactants, the time dependent concentrations follow the equations

\[ X'(t) = k_1 AY + k_2 AX - k_3 XY - 2k_4 X^2 \]
\[ Y'(t) = -k_1 AY - k_3 XY + (y/2)k_3 BZ \]
\[ Z'(t) = 2k_2 AX - k_5 BZ \]

J.J.Tyson (J. Phys. Chem. 1982) nondimensionalized this model using
The dimensionless Belusov-Zhabotinsky model is

\[\begin{align*}
\varepsilon x'(\tau) &= qy - xy + x(1 - x) \\
\eta y'(\tau) &= -qy - xy + yz \\
z'(\tau) &= x - z
\end{align*}\]

\(a)\) Find the steady-states of \(x\), \(y\), and \(z\): \(x_{ss}, y_{ss}\), and \(z_{ss}\).

\(b)\) Rewrite the system ODEs as a system of equations for the deviation variables, e.g. \(x(t) = x_{ss} + \delta_x(t)\). Assuming the deviations are much smaller than the steady state values, you can omit terms that correspond to squared deviations. In other words, you can assume that terms like \(\delta_x(t)^2\) and \(\delta_x(t)\delta_y(t)\) are negligible. A system of linear first order ODEs results. Find the matrix \(A\) so that you can write them as: \(d\delta/d\tau = A\delta\)

\(c)\) Explain how you would identify steady states as stable, or unstable. How would you identify oscillatory behavior of the solutions from the properties of \(A\)?

4) Recommended practice (answers given)

\(\text{H}_2^+\) is the simplest molecule. Many of its properties can be understood exactly. We will use simple integrals with basis functions that approximate the atomic orbitals of a Hydrogen atom. We'll use Gaussian basis functions to enable hand-calculations.

\(a)\) Normalize a 1s Gaussian orbital (in three-dimensions) for a Hydrogen atom. Remember, the normalization condition is that \(\langle \psi / \psi \rangle = 1\).

\(\psi_{1s}(r) = A(\xi) \exp[-\xi r^2]\)

\(b)\) Choose the constant \(\xi\) in the Gaussian orbital to maximize the overlap with a normalized Slater 1s orbital.

\(\varphi_{\text{slater}}(r) = \frac{1}{\sqrt{\pi}} \exp[-r]\)

\(c)\) Let a normalized 1s Gaussian orbital be centered on each of the two nuclei of \(\text{H}_2^+\). If the nuclei are at \(z = -d/2\) and \(z = +d/2\), with \(x=y=0\), then compute the overlap between the two normalized atomic orbitals separated by a distance \(d\). Hint:
\[ \psi_{1s}[(x^2 + y^2 + (z \pm d/2)^2)^{1/2}] \] Also, if you can't do this one, then don't worry. You won't actually need it for parts (d) and (e).

**d)** Let the overlap from part (c) be denoted \( S(d) \). Use your result to normalize the symmetric ("bonding") molecular orbital of \( \text{H}_2^+ \).

\[
\phi_{M.O.} \propto \psi_{1s}[(x^2 + y^2 + (z + d/2)^2)^{1/2}] + \psi_{1s}[(x^2 + y^2 + (z - d/2)^2)^{1/2}]
\]

**e)** Show that the bonding molecular orbital is orthogonal to the anti-bonding molecular orbital:

\[
\phi_{M.O.}^b \propto \psi_{1s}[(x^2 + y^2 + (z + d/2)^2)^{1/2}] - \psi_{1s}[(x^2 + y^2 + (z - d/2)^2)^{1/2}]
\]
3. a) **Normalize a 1s Gaussian orbital** $\psi_{1s}(r) = A(\xi) \exp[-\xi \cdot r^2]$

Remembering way back to quantum or physical chemistry, the wavefunction, $\psi(r)$, which expresses the space-time position of a particle, is not directly observable, but it can be related to observable properties. For instance, the probability distribution of the location of an electron can be expressed in terms of $\psi(r)$ and its complex conjugate, $\psi^*(r)$:

$$P(R \leq r \leq R + \Delta R) = \int_{R}^{R+\Delta R} \psi^*(r) \cdot \psi(r) \cdot 4\pi \cdot r^2 \, dr$$

It follows that since the probability of finding the electron anywhere in all of space is unity, the wavefunction $\psi(r)$ must be normalized such that:

$$\int_{0}^{\infty} \psi^*(r) \cdot \psi(r) \cdot 4\pi \cdot r^2 \, dr = 1$$

This can also be expressed as $\langle \psi^*(r) \vert \psi(r) \rangle = 1$ or in this case $\langle \psi_{1s}(r) \vert \psi_{1s}(r) \rangle = 1$ since $\psi_{1s}(r) = A(\xi) \exp[-\xi r^2]$ is purely real.

$$\langle \psi_{1s}(r) \vert \psi_{1s}(r) \rangle = \int_{0}^{\infty} A(\xi) \exp[-\xi r^2] \cdot A(\xi) \exp[-\xi r^2] \cdot 4\pi \cdot r^2 \, dr = 1$$

$$\langle \psi_{1s}(r) \vert \psi_{1s}(r) \rangle = 4\pi A^2 \int_{0}^{\infty} r \cdot \exp[-2\xi r^2] \, dr = 1$$

This can be evaluated using integration by parts:

Remember: $\int_{a}^{b} u \cdot dv = uv|_{a}^{b} - \int_{a}^{b} v \cdot du$

Let’s let $u = r$ and $dv = \exp[-2\xi r^2] \, dr$

This gives us $du = dr$ and $v = \frac{-1}{4\xi} \exp[-2\xi r^2]$

The integral above becomes:

$$1 = 4\pi A^2 \left[ \frac{-r}{4\xi} \exp[-2\xi r^2] \Bigg|_{0}^{\infty} + \frac{1}{4\xi} \int_{0}^{\infty} \exp[-2\xi r^2] \, dr \right]$$

Evaluating each term gives:

$$\frac{-r}{4\xi} \exp[-2\xi r^2] \Bigg|_{0}^{\infty} = -\infty \cdot \exp[-\infty^2] + 0 \cdot \exp[0] = 0$$

$$\int_{0}^{\infty} \exp[-2\xi r^2] \, dr = \frac{\sqrt{\pi}}{2} \frac{1}{\sqrt{2\xi}} \text{erf} \left[ \frac{\sqrt{2\xi}}{2} \right] = \frac{\sqrt{\pi}}{2\sqrt{2\xi}}$$

Plugging it in, we get:

$$1 = 4\pi A^2 \left[ 0 + \frac{1}{4\xi} \frac{\sqrt{\pi}}{2\sqrt{2\xi}} \right] = A^2 \left( \frac{\pi}{2\xi} \right)^{3/2}$$
\[ A = \left( \frac{2\xi}{\pi} \right)^{\frac{3}{4}} \]

\[ \psi_{1s}(r) = \left( \frac{2\xi}{\pi} \right)^{\frac{3}{4}} \exp[-\xi r^2] \]

**b) Find** \( \xi \) **that maximizes overlap between** \( \psi_{1s}(r) = A(\xi) \exp[-\xi r^2] \) **and**

\[ \varphi_{\text{Slater}}(r) = \frac{1}{\sqrt{\pi}} \exp[-r] \]

First we want to find an expression for the overlap as a function of \( \xi \). We know that the overlap is equal to the inner product of the two wavefunctions, \( \langle \varphi_{\text{Slater}}(r) | \psi_{1s}(r) \rangle \).

\[
\langle \varphi_{\text{Slater}}(r) | \psi_{1s}(r) \rangle = \int_0^\infty \varphi(r) \cdot \psi(r) \cdot 4\pi \cdot r^2 \, dr
\]

\[
\langle \varphi_{\text{Slater}}(r) | \psi_{1s}(r) \rangle = \int_0^\infty \frac{1}{\sqrt{\pi}} \exp[-r] \cdot \left( \frac{2\xi}{\pi} \right)^{\frac{3}{4}} \exp[-\xi r^2] \cdot 4\pi \cdot r^2 \, dr
\]

\[
\langle \varphi_{\text{Slater}}(r) | \psi_{1s}(r) \rangle = 4\sqrt{\pi} \left( \frac{2\xi}{\pi} \right)^{\frac{3}{4}} \int_0^\infty \exp[-r - \xi r^2] \cdot r^2 \, dr
\]

Now we want to find the maximum value of this function with respect to \( \xi \), or

\[
\frac{d}{d\xi} \langle \varphi_{\text{Slater}}(r) | \psi_{1s}(r) \rangle = 0
\]

\[
\frac{d}{d\xi} \langle \varphi_{\text{Slater}}(r) | \psi_{1s}(r) \rangle = 4\sqrt{\pi} \left( \frac{2\xi}{\pi} \right)^{\frac{3}{4}} \int_0^\infty -r^2 \exp[-r - \xi r^2] \cdot r^2 \, dr + 3\sqrt{\pi} \left( \frac{2\xi}{\pi} \right)^{\frac{3}{4}} \frac{2}{\pi} \int_0^\infty \exp[-r - \xi r^2] \cdot r^2 \, dr
\]

\[
\frac{d}{d\xi} \langle \varphi_{\text{Slater}}(r) | \psi_{1s}(r) \rangle = \int_0^\infty \left( -\frac{4\xi}{3} r^4 + r^2 \right) \exp[-r - \xi r^2] \, dr = 0
\]

Using Mathematica to solve this nasty equation for \( \xi \), we get:

\[ \xi \approx 0.27 \]
c. Compute the overlap between the two normalized Gaussian orbitals separated by distance \( d \).

It is apparent that this will require a change of coordinate systems if we hope to do any portion of this by hand. Since the primary coordinates of interest are \( z \) and \( r \), it makes the most sense to choose cylindrical coordinates.

If we call \( r_+ \) and \( r_- \) the distance away from the nuclei at \( z = +\frac{d}{2} \) and \( z = -\frac{d}{2} \), respectively, then \( r_+ \) and \( r_- \) can be represented in cylindrical coordinates by:

\[
r_+ = \sqrt{R^2 + z^2 + \frac{d^2}{4} - zd} \quad \text{and} \quad r_- = \sqrt{R^2 + z^2 + \frac{d^2}{4} + zd}
\]

To compute the overlap, we take the inner product

\[
\langle \psi_{13}(r_+) | \psi_{13}(r_-) \rangle = \int_{-\infty}^{\infty} \int_{0}^{\infty} \psi_{13}(r_+) \cdot \psi_{13}(r_-) \cdot 2\pi \cdot RdRdz
\]

\[
\langle \psi_{13}(r_+) | \psi_{13}(r_-) \rangle = \left( \frac{2\xi}{\pi} \right)^{\frac{3}{2}} \exp\left[ -\xi d^2 \right] \cdot 2\pi \int_{-\infty}^{\infty} \exp\left[ -2\xi \xi_0^2 \right] \cdot \frac{\sqrt{\pi}}{2\sqrt{2\xi}} \cdot \frac{1}{4\xi} \exp\left[ -2\xi R^2 \right] R dR
\]

\[
\langle \psi_{13}(r_+) | \psi_{13}(r_-) \rangle = \exp\left[ -\frac{\xi d^2}{2} \right] \equiv S(d)
\]
d. Normalize the bonding orbital $\phi_{MO} \propto (\psi_{1s}(r_+) + \psi_{1s}(r_-))$

$\phi_{MO} = B \cdot (\psi_{1s}(r_+) + \psi_{1s}(r_-))$

To normalize, set $\langle \phi_{MO} | \phi_{MO} \rangle = 1$

$$\langle \phi_{MO} | \phi_{MO} \rangle = \int_{\text{all space}} \phi_{MO} \cdot \phi_{MO} dV = \int B \cdot (\psi_{1s}(r_+) + \psi_{1s}(r_-)) \cdot B \cdot (\psi_{1s}(r_+) + \psi_{1s}(r_-)) dV$$

$$\langle \phi_{MO} | \phi_{MO} \rangle = B^2 \left( \int (\psi_{1s}(r_+))^2 + 2(\psi_{1s}(r_+) \cdot \psi_{1s}(r_-)) + (\psi_{1s}(r_-))^2 \right) dV = 1$$

$$\langle \phi_{MO} | \phi_{MO} \rangle = B^2 \left( 2 + 2S(d) \right) = 1$$

$$B = \frac{1}{\sqrt{2}} \left( 1 + S(d) \right)^{-\frac{1}{2}}$$

$$B = \frac{1}{\sqrt{2}} \left( 1 + \exp \left( -\frac{d^2}{2} \right) \right)^{-\frac{1}{2}}$$

$$\phi_{MO} = \frac{1}{\sqrt{2}} \left( 1 + \exp \left( -\frac{d^2}{2} \right) \right)^{-\frac{1}{2}} (\psi_{1s}(r_+) + \psi_{1s}(r_-))$$

e. Show that the bonding and anti-bonding orbitals are orthogonal.

$\phi_{MO}'' = C \cdot (\psi_{1s}(r_+) - \psi_{1s}(r_-))$

If orthogonal, $\langle \phi_{MO} | \phi_{MO}'' \rangle = 0$

$$\langle \phi_{MO} | \phi_{MO}'' \rangle = \langle \psi_{1s}(r_+) + \psi_{1s}(r_-) | \psi_{1s}(r_+) - \psi_{1s}(r_-) \rangle$$

$$\langle \phi_{MO} | \phi_{MO}'' \rangle = \int B \cdot (\psi_{1s}(r_+) + \psi_{1s}(r_-)) \cdot C \cdot (\psi_{1s}(r_+) - \psi_{1s}(r_-)) dV$$

$$\langle \phi_{MO} | \phi_{MO}'' \rangle = BC \int (\psi_{1s}(r_+))^2 + (\psi_{1s}(r_) \cdot \psi_{1s}(r_-)) - (\psi_{1s}(r_+) \cdot \psi_{1s}(r_-)) - (\psi_{1s}(r_-))^2 dV$$

$$\langle \phi_{MO} | \phi_{MO}'' \rangle = BC \int (\psi_{1s}(r_+))^2 - (\psi_{1s}(r_-))^2 dV$$

$$\langle \phi_{MO} | \phi_{MO}'' \rangle = BC(1-1)$$

$$\langle \phi_{MO} | \phi_{MO}'' \rangle = 0 \quad \leftrightarrow \quad \phi_{MO}'' \text{ and } \phi_{MO} \text{ are orthogonal.}$$