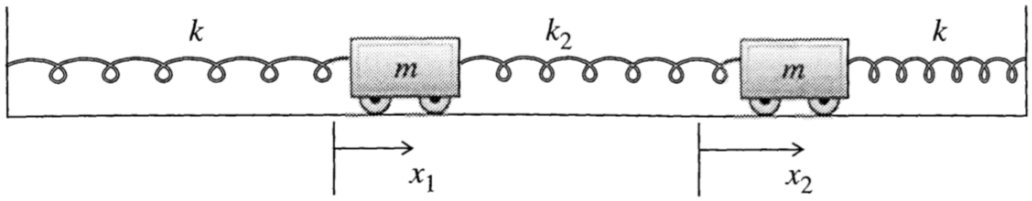
Problem Set 4

Note: The problems labeled with a star (★) are somewhat lengthy or tricky in the derivations. You are encouraged but not obligated to solve them for extra credits.

Lecture 12

Question 1. We can use the following classical toy model to examine the behavior of the solute molecules in a solvent (in one-dimensional space):



A solute molecule as a whole is represented by a cart with mass $m = 1$ (natural unit). Let us consider two neighboring solute molecules as two frictionless carts which are connected by a spring (with a force constant k_2, which characterizes the weak interaction between these two solute molecules). The interaction between the surrounding solvent and the solute molecule is represented by a spring (with a force constant k) connecting the solute (cart) with a fixed wall (environment).

(1) Solve for the normal-mode frequencies and the corresponding displacements of the solute molecules as a function of time $x_1(t)$, $x_2(t)$ (i.e., the particular solutions correspond to the normal mode).

(2) Let us set the phase angle to be zero, and $k = 9$, $k_2 = 1$ (natural unit). At time $t = 0$, the solute molecule on the left is away from the equilibrium position by A, i.e., $x_1 = A > 0$, and the solute molecule on the right is at its equilibrium position, i.e., $x_2 = 0$. Consider the general solutions $x_1(t)$ and $x_2(t)$ now. Plot $x_1(t)$, $x_2(t)$ with respect to t (please cover at least for $t = 0 – 100$).

(3) Following question (2), now express the motions in terms of the normal coordinates $Q_1(t)$, $Q_2(t)$. Plot $Q_1(t)$ and $Q_2(t)$, and analyze what you have seen in question (2).

Question 2. A diatomic molecule AB is confined on a 2D plane.

(1) Let us first consider a *fixed* Cartesian coordinate system (i.e., it does NOT rotate or translate with the molecule), of which the origin is NOT on the molecule. The mass for atom A is m_1 and atom B is m_2, and the potential energy function $V = \frac{1}{2}k\left|\boldsymbol{r}_1 - \boldsymbol{r}_2\right|^2$, in which $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the position

vectors for A and B respectively.

(a) Please construct the Hessian matrix by using the mass-weighted Cartesian coordinates (2D plane), and solve for all the normal modes and the corresponding frequencies.

(b) Can you identify the character of each mode? How many non-zero-frequency modes do you have? Is this consistent with your expectation for a linear molecule in 2D space?

(c) For the non-zero-frequency modes, which atom has a larger Cartesian-coordinate displacement, the heavier atom or the lighter atom?

(2) Next, let us consider a Cartesian coordinate system sticking to the molecule (rotating and translating with the molecule) with the origin being at the center of mass and the *x*-axis as the bond axis A–B. Construct the Hessian matrix by using the mass-weighted Cartesian coordinates again, and solve for the normal modes. Does the choice of the coordinate system affect the actual vibrational frequency?

Lecture 13

Question 3. (1) Consider $I = \int F\left[y(x), y'(x)\right]dx$, please show that if F does not explicitly depend on x, then the Euler-Lagrange equation can be written as: $y'\dfrac{\partial F}{\partial y'} - F = c$, in which c is a constant.

Hint: Start from $\dfrac{d}{dx}\left(y'\dfrac{\partial F}{\partial y'}\right)$ and substitute $\dfrac{d}{dx}\left(\dfrac{\partial F}{\partial y'}\right)$ with $\dfrac{\partial F}{\partial y}$ (Euler-Lagrange equation); and then consider the total derivative of $F(y, y', x)$.

★(2) Prove that the shortest distance between two points on the surface of a sphere lies on a great circle.

Hint: Use the spherical coordinates to express the distance between two points on a sphere as a line integral (note: on a given sphere with a fixed radius r, $dr = 0$), and then use the result in question (1) to show that the equation obtained from the variational principle represents a plane that passes through the center of the sphere.

Useful integral: $\int\left[a^2\sin^4\theta - \sin^2\theta\right]^{-1/2}d\theta = -\arcsin\dfrac{\cot\theta}{\left[a^2-1\right]^{1/2}} + c$

(3) Determine the curve (in the first quadrant) of a fixed length which passes through the points (0, 0) and (1, 0) and for which the area between the curve and the x axis is a maximum.

Question 4. Let us determine the path that minimizes the time that a particle will take to reach a lower point B along a flexible, frictionless wire under the force of gravity if it is released from rest from a higher point A.

(1) Set an upside-down coordinate system, i.e., the lower point B has larger (positive) y value than the higher point A, so that mgy represents the loss of the potential energy. Show that the optimal curve $y(x) = 0$ satisfies the following differential equation:

$$dx = \left(\frac{y}{c - y} \right)^{1/2} dy$$

(2) Validate that the parametrized curve $\begin{cases} x = \frac{c}{2}(\theta - \sin\theta) \\ y = \frac{c}{2}(1 - \cos\theta) \end{cases}$ satisfies the above differential equation. This curve is called a cycloid, which can be viewed as the curve traced by a point on the rim of a rolling cycle.

Question 5. Evaluate the functional variation $\frac{\delta E[\rho(\boldsymbol{r})]}{\delta \rho(\boldsymbol{r})}$ for the energy functional

$$E[\rho(\boldsymbol{r})] = c\int \rho(\boldsymbol{r})^{5/3} d\boldsymbol{r} + \int \rho(\boldsymbol{r}) v(\boldsymbol{r}) d\boldsymbol{r} + \frac{1}{2}\iint \frac{\rho(\boldsymbol{r}_1)\rho(\boldsymbol{r}_2)}{r_{12}} d\boldsymbol{r}_1 d\boldsymbol{r}_2 \quad .$$

Lecture 14

Question 6. Let $|\phi\rangle$ be the ground-state trial function and $|\psi_1\rangle$ the exact ground state, both of which are normalized. Consider the deviation of $|\phi\rangle$ from $|\psi_1\rangle$: $\Delta = 1 - |\langle \psi_1 | \phi \rangle|^2$. Please prove: $E - E_1 \geq (E_2 - E_1)\Delta$, where the variational energy $E = \langle \phi | \hat{H} | \phi \rangle$, the exact ground-state energy $E_1 = \langle \psi_1 | \hat{H} | \psi_1 \rangle$ and the exact first excited-state energy $E_2 = \langle \psi_2 | \hat{H} | \psi_2 \rangle$.

Question 7. A particle is trapped in a 1D box $-a \le x \le a$ with infinitely high potential walls. Consider the following trial function:

$$\phi(x) = \begin{cases} N(a^2 - x^2)(a^2 - \lambda x^2) & |x| < a \\ 0 & |x| \ge a \end{cases}$$

in which N is the normalization constant, and λ is the variational parameter. Calculate the variational ground-state energy, and compare its value to the exact one.

Question 8. In nuclear chemistry, the interaction between a proton and a neutron inside a deuterium (D) nucleus can be described by: $V(r) = -V_0 e^{-r/a}$, in which $V_0 = 32.7$ MeV, $a = 2.16$ fm.

Consider using the hydrogen 1*s* orbital as the trial function, i.e., $\phi(r) = Ne^{-\frac{\lambda r}{2a}}$ in which λ is the variational parameter and N the normalization constant. Calculate: (1) The variational ground-state energy; (2) The most probable radius; (3) The expectation value of the radius.

Note: This two-body problem is equivalent to a single particle with the mass being the reduced mass of a proton and a neutron, i.e., $\mu = m_P m_N/(m_P+m_N)$, under the central potential $V(\boldsymbol{r})$. The experimental ground-state energy for the D nucleus is – 2.23 MeV.

Hint: (a) Do not forget that you will need to do the integrals in the spherical coordinate

$$d\tau = r^2 sin\theta dr d\theta d\phi$$

(b) Laplacian in the spherical coordinate

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial \theta}\left(sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{r^2 sin^2\theta}\left(\frac{\partial^2}{\partial \varphi^2}\right)$$

(You do not have angular part in your trial function!)

(c) Use a numerical program (e.g., MATLAB) to solve a quartic algebraic equation.

(d) Useful integral: By integrating by part successively, one can show the following (n: an integer)

$$\int_0^{+\infty} x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$$

★**Question 9.** In this question, we examine the relation between the eigenvalues of a Hermitian matrix and its submatrices, and prove Cauchy's interlace theorem. Consider the D by D matrix **M**

and its d by d submatrix $\mathbf{m}$:

$$\mathbf{M} = \begin{pmatrix} \mathbf{m} & \mathbf{V} \\ \mathbf{V}^\dagger & \mathbf{W} \end{pmatrix}$$

We denote the orthonormal eigenvectors of $\mathbf{M}$ by $\mathbf{B}_1$, $\mathbf{B}_2$, ..., $\mathbf{B}_D$ and the eigenvalues by $E_1 \le E_2 \le \cdots \le E_D$. Likewise, for the orthonormal eigenvectors and the eigenvalues of $\mathbf{m}$, we use the notation $\mathbf{b}_1$, $\mathbf{b}_2$, ..., $\mathbf{b}_d$ and $e_1 \le e_2 \le \cdots \le e_d$. In the following, we shall regard the eigenvectors $\mathbf{b}_k$ as vectors in the full D-dimensional space, with the last $D - d$ elements set equal to 0. The eigenvectors $\mathbf{b}_k$ may then be expanded in the eigenvectors $\mathbf{B}_K$ in the usual manner: $\mathbf{b}_k = \sum_{K=1}^{D} a_K \mathbf{B}_K$.

(1) Show that the lowest eigenvalue of $\mathbf{m}$ is an upper bound to the lowest eigenvalue of $\mathbf{M}$: $E_1 \le e_1$

(2) Show that $\dfrac{\mathbf{X}^\dagger \mathbf{M} \mathbf{X}}{\mathbf{X}^\dagger \mathbf{X}} \ge E_i$ in which $\mathbf{X}$ is orthogonal to all $\mathbf{B}_K$ with $K < i$.

(3) Assume that the square matrix containing $\mathbf{B}_K^\dagger \mathbf{b}_k$ with $1 \le K < i$ and $1 \le k < i$ is nonsingular. Show that the coefficients a_k in the expression $\mathbf{c}_i = \mathbf{b}_i + \sum_{k=1}^{i-1} a_k \mathbf{b}_k$ can be chosen such that $\boldsymbol{c}_i$ becomes orthogonal to all $\mathbf{B}_K$ with $K < i$.

(4) Using (2) and (3), show that, for $1 < i \le d$, the inequality $E_i \le e_i$ holds if the matrix containing $\mathbf{B}_K^\dagger \mathbf{b}_k$ with $1 \le K < i$ and $1 \le k < i$ is nonsingular.

(5) Show that the highest eigenvalue of $\mathbf{M}$ is an upper bound to the highest eigenvalue of $\mathbf{m}$: $e_d \le E_D$. Also show that, for $1 \le i < d$, the inequality $e_{d-i} \le E_{D-i}$ holds if the matrix containing $\mathbf{B}_{D-K}^\dagger \mathbf{b}_{d-k}$ with $0 \le K < i$ and $0 \le k < i$ is nonsingular.

(6) Show that, under the usual assumptions, the above results imply the inequalities $E_i \le e_i \le E_{i+D-d}$ and that, for the special case of $d = D - 1$, we obtain

$$E_1 \le e_1 \le E_2 \le e_2 \le E_3 \le \cdots \le E_d \le e_d \le E_{d+1}$$

Lecture 15

Question 10. In this question, let us consider the variational treatment of a 1D Helium atom. The electrons are constrained in 1D space, and the electron-nucleus and electron-electron interactions are approximated by the Dirac delta functions. The electrons in the 1D Helium atom are governed

by the following Hamiltonian: $\hat{H} = -\frac{1}{2}\left(\frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} \right) - Z\left[\delta(x_1) + \delta(x_2) \right] + \delta(x_1 - x_2)$, in which x_1 and x_2 are the coordinates of electron 1 and 2, and Z is the nuclear charge for the Helium atom (Z = +2). Use the normalized trial function $\phi(x_1, x_2) = \lambda e^{-\lambda(|x_1|+|x_2|)}$, in which λ is the variational parameter (the effective nuclear charge felt by an electron), determine the ground-state energy.

Useful integral: $\int_{-\infty}^{+\infty} \left| \frac{d}{dx} e^{-a|x|} \right|^2 dx = a$

Question 11. Calculate the resonance integral (in atomic unit) for H_2^+ in the minimal basis: $\left\langle 1s_A \middle| \hat{H} \middle| 1s_B \right\rangle$ (Express your result in terms of the internuclear distance R only.)

Question 12. Consider a linear H_3 molecule. The wavefunctions may be modelled by expressing them as $\psi = c_A s_A + c_B s_B + c_C s_C$, in which s_i denotes the hydrogen 1s orbital of the relevant atom.

Let us assume that $H_{ij} = \begin{cases} \alpha & (i = j) \\ \beta & (i, j \text{ are neighbours}) \\ 0 & (i, j \text{ are not neighbours}) \end{cases}$ and the overlap matrix $\boldsymbol{S}$ is an identity matrix. Solve for the energy levels variationally (in terms of the parameters α and β), and schematically plot the corresponding molecular orbitals.

Question 13. In this question, we shall prove that the variationally determined approximated electronic wavefunction of a molecule satisfies the virial theorem: $2\langle T \rangle + \langle V \rangle = 0$, in which T is the total kinetic energy operator including the nuclear motions.

(1) Write down the electronic Hamiltonian of a molecule.

(2) Scale the coordinates $\boldsymbol{r}_i$ to $\boldsymbol{r}_i/\alpha$ (for electrons), and $\boldsymbol{R}_N$ to $\boldsymbol{R}_N/\alpha$ (for nuclei). Write down the expression for the expectation value of energy $\langle E(\alpha) \rangle$.

(3) Set α = 1, we recover the expectation value of energy $\langle E \rangle = \langle T \rangle + \langle V \rangle$. Show that at the variational extremum with α = 1, we arrived at the virial theorem.