Project: Vibration of Diatomic Molecules

Objective: Find the vibration energies and the corresponding vibrational wavefunctions of diatomic molecules H_2 and I_2 using the Morse potential.

Required Numerical Methods:

- Root finding

- Numerical Integration

- ODE - Eigenvalue problems

- Special Functions (Laguerre polynomials)

Tasks

1. Evaluate the analytic expression of energy eigenvalue and eigenfunction.

2. Find the energy eigenvalue using the Bohr-Somerfeld semi quantization rule.

3. Find the energy eigenvalue and wavefunction of the ground state by integrating Schrödinger equation numerically. Choose one of the methods specified below.

1 Physical Background

The Hamiltonian for a diatomic molecule is given by

$$\mathcal{H} = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \frac{Z_1 Z_2 e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} + \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_i \sum_{j>i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \left[\frac{Z_1 e^2}{|\mathbf{r}_i - \mathbf{R}_1|} + \frac{Z_2 e^2}{|\mathbf{r}_i - \mathbf{R}_2|} \right] \quad (1)$$

where $\mathbf{R}_i$, $\mathbf{P}_i$, and Z_i are the position, linear momentum, and charge of the nuclei, respectively, and $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and momentum of electrons, respectively.

Since the nuclei are much heavier than the electrons, the electrons move fast enough to readjust their wavefunctions instantaneously to the change of nuclear positions. In such a case, the electronic state can be calculated by freezing nuclear motion (Born-Oppenheimer Approximation). Then, the Schrödinger equation for the electrons is given by

$$\left[\sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_i \sum_{j>i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_i \left\{ \frac{Z_1 e^2}{|\mathbf{r}_i - \mathbf{R}_1|} + \frac{Z_2 e^2}{|\mathbf{r}_i - \mathbf{R}_2|} \right\} \right] \Phi_k(\mathbf{r}_1, \cdots, \mathbf{r}_N) = E_k(\mathbf{R}_1, \mathbf{R}_2)\Phi_k(\mathbf{r}_1, \cdots, \mathbf{r}_N)$$

$$(2)$$

Here the energy E_k is a function of the nuclear position. However, the nuclear positions are not dynamical variables but merely parameters in this equation. Due to the cylindrical symmetry, E_k depends only on the distance between the nuclei.

Averaging the total Hamiltonian (1) over the electron coordinates, one can obtain the effective Hamiltonian for the nuclei,

$$\mathcal{H}_N \;=\; \langle \Phi_k \mid \mathcal{H} \mid \Phi_k \rangle \tag{3}$$

$$\;=\; \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + U_k(\mid \mathbf{R}_1 - \mathbf{R}_2 \mid) \tag{4}$$

where U_k is an interaction potential defined as

$$U_k(R) = \frac{Z_1 Z_2 e^2}{R} + E_k(R) \tag{5}$$

Using the center-of-mass frame, the relative motion of the nuclei is described by the single-particle Schrödinger equation

$$\left[\frac{P^2}{2\mu} + U_k(R) \right] \Phi(R) = \lambda \Phi(R). \tag{6}$$

where μ is a reduced mass. Now, since this equation has spherical symmetry, the dimension of the equation can be reduced by introducing a radial wave function $\chi(R)$ by $\Psi(\mathbf{R}) = \frac{\chi(R)}{R} Y_{\ell,m}(\theta, \phi)$. The radial function satisfies the 1D Schrödinger equation

$$-\frac{\hbar^2}{2\mu} \frac{d^2 \chi}{dr^2} + \left[U_k(R) + \frac{\hbar^2 \ell(\ell+1)}{R} \right] \chi = \lambda \chi. \tag{7}$$

Note that χ depends on both the electronic state k and the rotational motion ℓ.

Since it is very hard to solve Eq. (2), an empirical form of $U_k(R)$ is often used. The most popular potentials are,

- Lennard-Jones Potential
$$U(R) = 4D_e \left[\left(\frac{a}{R} \right)^{12} - \left(\frac{a}{R} \right)^{6} \right] \tag{8}$$

- Morse Potential

$$U(R) = D_e \left[\exp(-2\alpha(R - R_0)) - 2\exp(-\alpha(R - R_0)) \right] \tag{9}$$

In this project, the Morse potential is used to calculate H_2 and I_2 molecules. The constants for these molecules are given in Table 1.

Table 1: Values of the constants for the Morse potential.

Molecule	R_0(Å)	D_e (eV)	αR_0
H_2	0.742	4.75	1.44
I_2	2.66	1.56	4.94

2 Exact Analytical Solution

The Schrödinger equation for a particle bound in the Morse potential,

$$\frac{d^2\phi}{dx^2} + \frac{2\mu}{\hbar}\left(\lambda - D_e e^{-2\alpha x} + 2D_e e^{-\alpha x}\right)\psi = 0,$$

can be solved analytically. Here $x = R - R_0$. Introducing new variables,

$$\xi = \frac{2\sqrt{2\mu D_e}}{\alpha\hbar}e^{-\alpha x}, \quad s = \frac{\sqrt{-2\mu\lambda}}{\alpha\hbar}, \quad n = \frac{\sqrt{2\mu D_e}}{\alpha\hbar} - \left(s + \frac{1}{2}\right),$$

the Schrödinger equation is expressed as

$$\psi'' + \frac{\psi'}{\xi} + \left(-\frac{1}{4} + \frac{n + s + \frac{1}{2}}{\xi} - \frac{s^2}{\xi^2}\right)\psi = 0.$$

Taking into account the asymptotic solutions, $e^{-\xi/2}$ for $\xi \to \infty$ and ξ^s for $\xi \to 0$ a general solution is conveniently written as

$$\psi = e^{-\xi/2}\xi^2 w(\xi)$$

where $w(\xi)$ should be a polynomial and satisfy the following equation:

$$\xi w'' + (2s + 1 - \xi)w' + nw = 0$$

which is a Laguerre equation. Using proper boundary conditions, we find a solution,

$$w = L_n^{(2s)}(\xi)$$

and an energy eigenvalue,

$$\lambda_n = -D_e\left[1 - \frac{\alpha\hbar}{\sqrt{2\mu D_e}}\left(n + \frac{1}{2}\right)\right]^2.$$

where n is zero or a positive integer. The number of bound states can be obtained from the inequality

$$\frac{\sqrt{2\mu D_e}}{\alpha\hbar} > n + \frac{1}{2}$$

The Laguerre polynomials can be evaluated easily using The recursive equation

$$nL_n^{(\alpha)}(x) + (x - 2n - \alpha + 1)L_{n-1}^{(\alpha)}(x) + (n + \alpha - 1)L_{n-2}^{(\alpha)}(x) = 0$$

and

$$L_0^{(\alpha)}(x) = 1, \quad L_1^{(\alpha)}(x) = 1 + \alpha - x$$

3

3   Bohr-Sommerfeld semiclassical quantization

We can find approximate quantum-mechanical energy using the Bohr-Sommerfeld semiclassical quantization rule, which determines the energies by the equation

$$S(\lambda_n) = 2\pi\hbar(n + \frac{1}{2}) \tag{10}$$

where the action S is defined as

$$S(\lambda) = \oint p(x)dx$$

and the momentum p is given as

$$p(x) = \pm\sqrt{2\mu(\lambda - U(x))}$$

For a one-dimensional system, we have the action integral

$$S(\lambda) = 2\int_{x_1}^{x_2} \sqrt{2\mu(\lambda - U(x))}dx \tag{11}$$

where x_1 and x_2 are the inner and outer classical turning points given as roots of $p(x) = 0$.

Our purpose is to find λ that satisfies Eq (10). This can be considered as a root finding problem. To solve this problem,

1. Guess λ (It does not have to be a good guess but it has to be between $-D_e$ and 0. Why?)

2. Find classical turning points by solving p(x) = 0. This is also a root finding problem. It is obvious that the inner turning point is negative and the outer is positive. We also know there are only two roots. Therefore, it is easy to bracket the roots.

3. Compute the action integral (11) using a numerical quadrature. If you want to use the Simpson method, watch out the boundary values.

4. Evaluate Eq (10) for a given n. If it is not satisfied, then the current λ is not a solution. How do you want change λ? Remember this is a root finding problem. The bisection method works but there are many roots depending on the potential depth and width. We must bracket them. Fortunately, λ takes value between $-D_e$ and 0. Therefore, we can use the exhaustive searching method.

4   Numerical Integration of Schrödinger Equation

4.1   Numerov Method

See the lecture note.

4.2 Steepest descent method

For a quantum system, $\mid \psi \rangle$, the energy, E, is given by the expectation value

$$E[\psi] = \langle \psi \mid \mathcal{H} \mid \psi \rangle \tag{12}$$

with the normalization condition

$$\langle \psi \mid \psi \rangle = 1 \tag{13}$$

An eigenstate of the system corresponds to a stationary point of the energy functional with respect to ψ. Using the Lagrange's multiplier, λ, for the normalization constraint (13, a stationary point can be obtained by taking the variation of $E[\psi]$ as follows:

$$
\begin{aligned}
0 &= \frac{\delta}{\delta \psi^*} \left\{ E[\psi] - \lambda \left(\langle \psi \mid \psi \rangle - 1 \right) \right\} \\
&= \mathcal{H} \mid \psi \rangle - \lambda \mid \psi \rangle
\end{aligned}
$$

(14)

(15)

which is nothing but a Schrödinger equation. Therefore, minimizing the energy functional (12) with respect to ψ under the normalization constraint (13) is equivalent to solving a Schrödinger equation. In practice, we can normalize ψ numerically and therefore, the Lagrange multiplier method is not necessary.

Suppose that the state vector, $\mid \psi \rangle$, is expressed using a vector $\vec{u} = (u_1 u_2 \cdots u_N)$ in a certain representation. For example, when the finite difference method is used, $u_i = \psi(x_i)$. Then, the energy expectation value is a function of $\vec{u}$. Starting with an initial vector $\vec{u}^{(0)}$, the energy can be minimized by the iterative procedure (the steepest descent method)

$$\vec{u}^{(n+1)} = \vec{u}^{(n)} - \xi \nabla E(\vec{u}^{(n)}) \tag{16}$$

where ξ is a parameter to control the convergency. When ξ is too large, the iteration diverges. At every iteration, $\vec{u}$ must be renormalized since this iteration not only its direction but also its norm. Alternatively, when the Lagrange's multiplier method is used,

$$\vec{u}^{(n+1)} = \vec{u}^{(n)} - \xi \nabla E(\vec{u}^{(n)}) + \xi \lambda \vec{u}^{(n)} \tag{17}$$

where the Lagrange's multiplier, λ, is determined by the normalization condition,

$$
\begin{aligned}
1 &= \vec{u}^{(n+1)} \cdot \vec{u}^{(n+1)} \\
&= \left| \vec{u}^{(n)} - \xi \nabla E(\vec{u}^{(n)}) + \xi \lambda \vec{n}^{(n)} \right|^2
\end{aligned}
$$

(18)

(19)

which guarantees that $\vec{u}$ is always normalized.

From the variational calculation (15), the gradient of $E(\vec{u})$ is given by

$$\frac{\partial}{\partial u_i} E(\vec{u}) = \sum_j \mathcal{H}_{ij} u_j \tag{20}$$

where $\mathcal{H}_{ij}$ is a matrix form of the Hamiltonian. For example, if the finite difference method is used, it is a tridiagonal matrix used in the previous section. The iteration is repeated until $\vec{u}$ does not change within a given tolerance.

The steepest descent method is simple and works. However, it is very often too slow depending on the landscape of the the energy functional, especially it has a deep valley. There are quite few other algorithms for minimization. The conjugate gradient method is one of them. The Lanczos method is also popular for large eigenvalue problems.

4.3 Imaginary time = Temperature

Consider a time-dependent Schrödinger equation

$$\imath\hbar\frac{\partial\psi(t)}{\partial t} = \mathcal{H}\psi(t). \tag{21}$$

A solution for an initial state, $\psi(0)$, is given by

$$\psi(t) = e^{-\imath\mathcal{H}t/\hbar}\psi(0). \tag{22}$$

Since this is a unitary transformation, the norm of ψ conserves. If the eigenvalues and eigenvectors of the Hamiltonian are all known, then Eq (22) is written as

$$\psi(t) = \sum_{n=1} e^{\imath E_n t/\hbar} c_n u_n \tag{23}$$

where

$$\mathcal{H}u_n = E_n u_n \tag{24}$$

and the expansion coefficient is defined by $c_n = \langle u_n \mid \psi \rangle$. Note that the probability of finding the system in a state u_n does not change in time.

Now, let us replace time with an imaginary parameter, $t = -\imath\hbar\beta$ ($\beta > 0$). Then, Eq (21) becomes

$$\frac{\partial\psi(\beta)}{\partial\beta} = -\mathcal{H}\psi(\beta) \tag{25}$$

and its solution is

$$\psi(\beta) = \sum_{n=1} e^{-E_n\beta} c_n u_n. \tag{26}$$

Suppose that the energy measured from the lowest energy state, $\tilde{E}_n = E_n - E_1$, then

$$\psi(\beta) = c_1 u_1 + \sum_{n=2} e^{-\tilde{E}_n\beta} u_n \tag{27}$$

Since $\tilde{E}_n > 0$, $\psi \to c_1 u_1$ as β goes to ∞. Therefore, $\psi(\infty)/c_1$ is the lowest eigenstate of the Hamiltonian.

Unfortunately, this method is useless because we have to measure the energy from the lowest eigenvalue which we are going to calculate. There is a way to get around this problem. If you measure the energy from an arbitrary origin, then $\mid \psi(\infty) \mid$ is either 0 or ∞ because the transformation

from $\psi(0)$ to $\psi(\beta)$ is no longer unitary. However, we can normalize $\psi(\beta)$ at any β

$$
\tilde{\psi}(\beta) = \frac{e^{-\mathcal{H}\beta}\psi(0)}{\sqrt{\langle\psi(\beta) \mid e^{-2\mathcal{H}\beta} \mid \psi(\beta)\rangle}} \tag{28}
$$

$$
= \frac{\displaystyle\sum_{n=1}e^{-E_n\beta}c_n u_n}{\sqrt{\displaystyle\sum_{n=1}e^{-2E_n\beta} \mid c_n \mid^2}} \tag{29}
$$

$$
= \frac{c_1 u_1 + \displaystyle\sum_{n=2}e^{-\tilde{E}_n\beta}c_n u_n}{\sqrt{\mid c_1 \mid^2 + \displaystyle\sum_{n=2}e^{-2\tilde{E}_n\beta} \mid c_n \mid^2}} \tag{30}
$$

$$
\rightarrow u_1 \quad (\beta \rightarrow \infty) \tag{31}
$$

Therefore, solving the differential equation (25) under the normalization constraint from $\beta = 0$ to ∞ gives the lowest-energy eigen state.

Using the Euler method, a numerical solution to Eq (25) is given by the recursive equation

$$
\psi(\beta_{n+1}) = \psi(\beta_n) - \Delta\beta\mathcal{H}\psi(\beta_n) \tag{32}
$$

where $\Delta\beta = \beta_{n+1} - \beta_n$. Compare this equation with Eqs (16 and (20). This method is nothing but a steepest descent method!

Another trick to solve Eq (25) is to measure the energy from the mean value,

$$
V = \frac{\langle\psi \mid \mathcal{H} \mid \psi\rangle}{\langle\psi \mid \psi\rangle} \tag{33}
$$

$$
= \frac{\displaystyle\sum_{n=1}E_n e^{-2E_n\beta} \mid c_n \mid^2}{\displaystyle\sum_{n=1}e^{-2E_n\beta} \mid c_n \mid^2} \tag{34}
$$

$$
> E_1 \tag{35}
$$

Then,

$$
\tilde{E}_n = E_n - V \tag{36}
$$

The states whose energy is higher than V vanish as β becomes large because their energies, $\tilde{E}_n$ are positive. On the other hand, the states below V grows exponentially because of the negative energies. Since V approaches E_0 as $\beta \rightarrow \infty$, only the lowest energy state survives at a large β. We use this scheme later in the diffusion Monte Carlo method.

This steepest descent method has a non-trivial physical background. The exponential factor $\exp(-E_n\beta)$ looks like a Boltzmann factor in the statistical mechanics if $\beta = 1/k_B T$ where T and k_B are temperature and the Boltzmann constant. At $T = \infty$ ($\beta = 0$), all eigenstates are mixed. As the temperature goes down, only low-energy states are occupied and at $T = 0$ ($\beta = \infty$) the system occupy only the lowest energy state. Therefore, the imaginary time can be interpreted as a temperature.