Homework 1 Solutions

Problem 1

Recall in the Born-Oppenheimer approximation for the two-proton, two-electron system that we expanded the total wave function in terms of the electronic wave functions ϕ_i. (See the notes on the class web page if you don't remember.) We then plugged this expansion into the Schrödinger wave equation for the whole system, multiplied by another electronic wave function, and integrated over the electronic coordinates. This left us with (using the notation from the class notes)

$$\iint d\mathbf{r} \left[\phi_j^*(\mathbf{r};\mathbf{R}) \left(T_p + T_e + U_{ee} + U_{ep} + U_{pp}\right) \sum_i \chi_{s,i}(\mathbf{R})\phi_i(\mathbf{r};\mathbf{R}) \right] =$$
$$E_s \iint d\mathbf{r}\, \phi_j^*(\mathbf{r};\mathbf{R}) \sum_i \chi_{s,i}(\mathbf{R})\phi_i(\mathbf{r};\mathbf{R}). \tag{1}$$

Note that while we are following the class notation, which was done for a hydrogen molecule, this easily generalized to the case of N protons because the proton configuration is frozen and described in $\mathbf{R}$. In the same way, we write the electronic coordinates as a set $\mathbf{r} = \{\mathbf{r}_i\}$. i and j index the electronic wave functions over which the inner product is being done. Moving on, because of the orthogonality of the electron wave functions, the right-hand side of this expression reduces to $E_s\chi_j(\mathbf{R})$. Furthermore, we defined the ϕ_i as eigenfunctions of $T_e + U_{ee} + U_{ep} + U_{pp}$ with eigenvalues $E_i(\mathbf{R})$. Therefore, our expression reduces to

$$\iint d\mathbf{r} \left[\phi_j^*(\mathbf{r};\mathbf{R}) T_p \sum_i \chi_{s,i}(\mathbf{R})\phi_i(\mathbf{r};\mathbf{R}) \right] + \chi_{s,j}(\mathbf{R})E_j(\mathbf{R}) = E_s\chi_{s,j}(\mathbf{R}). \tag{2}$$

The proton kinetic energy operator is all that remains. Recall that the kinetic energy operator (in general) is given by

$$T_p = -\frac{\hbar^2}{2m_p}\nabla^2 = -\frac{\hbar^2}{2m_p}\nabla\cdot\nabla. \tag{3}$$

(For this system, since we have two protons, we will have two such terms.) Consider the action of one of the kinetic energy operators on our expanded wave function. Dropping the coordinates for clarity, we have

$$\begin{aligned} \nabla_\alpha \cdot \nabla_\alpha \left(\chi_{s,i}\phi_i\right) &= \nabla_\alpha \cdot \left[\left(\nabla_\alpha\chi_{s,i}\right)\phi_i + \chi_{s,i}\nabla_\alpha\phi_i\right] \\ &= \left(\nabla_\alpha^2\chi_{s,i}\right)\phi_i + 2\left(\nabla_\alpha\chi_{s,i}\right)\left(\nabla_\alpha\phi_i\right) + \chi_{s,i}\nabla_\alpha^2\phi_i, \end{aligned} \tag{4}$$

where α is an index labeling the proton coordinates with which the derivatives are to be taken with respect to. As discussed in the notes, the first term is the kinetic energy of the

protons, and the second two terms, once we simplify and rearrange them, will constitute the non-adiabiticity operator. Plugging these two terms back into the integral, we have

$$
\begin{aligned}
&-\frac{\hbar^2}{2m_p}\iint d\mathbf{r}\ \left[\phi_j^*(\mathbf{r};\mathbf{R})\sum_{i,\alpha}\left[2\left(\nabla_\alpha\chi_{s,i}(\mathbf{R})\right)\left(\nabla_\alpha\phi_i(\mathbf{r};\mathbf{R})\right)+\chi_{s,i}(\mathbf{R})\nabla_\alpha^2\phi_i(\mathbf{r};\mathbf{R})\right]\right]\\
&=-\frac{\hbar^2}{2m_p}\iint d\mathbf{r}\ \left[\phi_j^*(\mathbf{r};\mathbf{R})\sum_{i,\alpha}\Big[\left(\nabla_\alpha\phi_i(\mathbf{r};\mathbf{R})\right)\nabla_\alpha+\nabla_\alpha^2\phi_i(\mathbf{r};\mathbf{R})\Big]\chi_{s,i}(\mathbf{R})\right]\\
&=-\frac{\hbar^2}{2m_p}\iint d\mathbf{r}\ \left[\sum_{i,\alpha}\Big[\phi_j^*(\mathbf{r};\mathbf{R})\left(\nabla_\alpha\phi_i(\mathbf{r};\mathbf{R})\right)\nabla_\alpha+\phi_j^*(\mathbf{r};\mathbf{R})\nabla_\alpha^2\phi_i(\mathbf{r};\mathbf{R})\Big]\chi_{s,i}(\mathbf{R})\right]\\
&=-\frac{\hbar^2}{2m_p}\sum_{i,\alpha}\Big[\left\langle\phi_j\,|\,\nabla_\alpha\,|\,\phi_i\right\rangle\nabla_\alpha+\left\langle\phi_j\,\middle|\,\nabla_\alpha^2\,\middle|\,\phi_i\right\rangle\Big]\chi_{s,i}(\mathbf{R})\\
&=\sum_\alpha C_{\alpha,j}\chi_{s,i}(\mathbf{R}),
\end{aligned}
\tag{5}
$$

where we have found the non-adiabaticity operator $C_{\alpha,j}$ to be

$$
\boxed{C_{\alpha,j}=-\frac{\hbar^2}{2m_p}\sum_i\Big[\left\langle\phi_j\,|\,\nabla_\alpha\,|\,\phi_i\right\rangle\nabla_\alpha+\left\langle\phi_j\,\middle|\,\nabla_\alpha^2\,\middle|\,\phi_i\right\rangle\Big]}
\tag{6}
$$

In the naive Born-Oppenheimer approximation, we only consider the electronic ground states. For $i=0$ and $j=0$ then, the non-adiabaticity operator becomes

$$
C_{\alpha,0}=-\frac{\hbar^2}{2m_p}\left\langle\phi_0\,|\,\nabla_\alpha\,|\,\phi_0\right\rangle\nabla_\alpha+\left\langle\phi_0\,\middle|\,\nabla_\alpha^2\,\middle|\,\phi_0\right\rangle.
\tag{7}
$$

To simplify the first term, first recall that the electronic wave functions are normalized, and then consider the gradient of the normalization condition:

$$
\begin{aligned}
\nabla_\alpha\left(\langle\phi_0\,|\,\phi_0\rangle\right)=\nabla_\alpha(1)&=0\\
&=\left(\nabla_\alpha\langle\phi_0|\right)|\phi_0\rangle+\langle\phi_0|\left(\nabla_\alpha|\phi_0\rangle\right)\\
&=2\left(\langle\phi_0|\,\nabla_\alpha\right)|\phi_0\rangle,
\end{aligned}
\tag{8}
$$

where we have made use of the Hermiticity of the operator. Thus, the first term vanishes, and in the naive Born-Oppenheimer the non-adiabaticity operator becomes

$$
\boxed{C_{\alpha,0}=-\frac{\hbar^2}{2m_p}\left\langle\phi_0\,\middle|\,\nabla_\alpha^2\,\middle|\,\phi_0\right\rangle}
\tag{9}
$$

This term is related to the response of the electronic states to a change in the nuclear configuration.

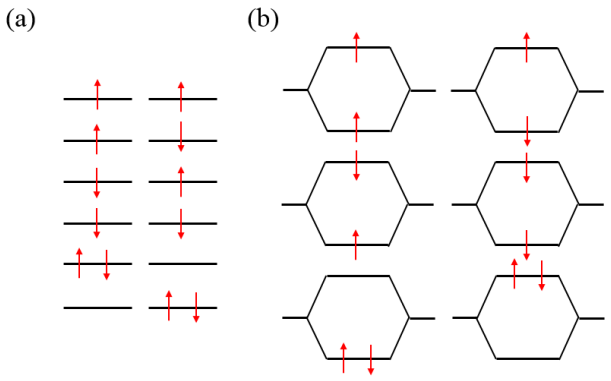

Figure 1: Basis states for the hydrogen molecule with $1s$ orbitals and spin in (a) the atomic and (b) molecular orbital bases.

Problem 2

(a) Diagrams of the atomic and molecular basis states for hydrogen with $1s$ orbitals and spin are shown in Figure 1. Two electrons can occupy four orbitals in six ways.

(b) In the molecular basis, the highest energy state is when both electrons are in the anti-bonding state. We will write this wave function in terms of the one-electron wave functions $\chi_1 = \psi_{\rm B}\alpha$, $\chi_2 = \psi_{\rm B}\beta$, $\chi_3 = \psi_{\rm AB}\alpha$, and $\chi_4 = \psi_{\rm AB}\beta$, where $\psi_{\rm B}$ and $\psi_{\rm AB}$ are the bonding and anti-bonding states and α and β are the spin orbitals. The electrons must have opposite spins to satisfy the Pauli exclusion principle, and because they are fermions, the wave function must be antisymmetric. Therefore, we can write the total wave function in the molecular picture using a Slater determinant composed of χ_3 and χ_4:

$$\Psi_{\rm mol}(\mathbf{r}_1,\,\omega_1;\,\mathbf{r}_2,\,\omega_2) = \frac{1}{\sqrt{2}}\begin{vmatrix}\psi_{\rm AB}(\mathbf{r}_1)\alpha(\omega_1) & \psi_{\rm AB}(\mathbf{r}_1)\beta(\omega_1)\\ \psi_{\rm AB}(\mathbf{r}_2)\alpha(\omega_2) & \psi_{\rm AB}(\mathbf{r}_2)\beta(\omega_2)\end{vmatrix}, \tag{10}$$

where the factor of $1/\sqrt{2}$ has been included for normalization. Expanding the determinant and simplifying, we have

$$\boxed{\Psi_{\rm mol}(\mathbf{r}_1,\,\omega_1;\,\mathbf{r}_2,\,\omega_2) = \frac{1}{\sqrt{2}}\psi_{\rm AB}(\mathbf{r}_1)\psi_{\rm AB}(\mathbf{r}_2)\left[\alpha(\omega_1)\beta(\omega_2) - \alpha(\omega_2)\beta(\omega_1)\right]} \tag{11}$$

In the atomic representation, all the states have equal energy. This would not be true if we allowed for electron interactions.

Problem 3

To solve this problem, we will follow the class notes on the Born-Oppenheimer approximation and on the harmonic approximation. Before we proceed, let us outline the procedure we will follow:

(i) Separate the wave function of the protons and the electrons.

(ii) Expand the total wave function in the basis of electronic states.

(iii) Use this to write Schrödinger's equation for the proton wave function.

(iv) Assume the potential for the protons is harmonic, and solve for the wave functions.

(v) Approximate the electronic wave function as an antisymmetric combination of single-electron wave functions.

The first three steps above are from the Born-Oppenheimer approximation. The Hamiltonian for this system is

$$\begin{aligned} H &= T_\mathrm{p} + H_\mathrm{el} \\ &= T_\mathrm{p} + T_\mathrm{e} + U_\mathrm{pp} + U_\mathrm{ee} + U_\mathrm{ep}. \end{aligned} \tag{12}$$

Let us denote the eigenstates of this Hamiltonian as $\Psi_s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)$, where the lowercase $\mathbf{r}_i$ denote the positions of the electrons and the $\mathbf{R}_i$ denote the positions of the nuclei. Treating the protons as stationary compared to the electrons, we first solve the electronic problem:

$$H_\mathrm{el}\varphi_i(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) = E_i(\mathbf{R})\varphi_i(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}), \tag{13}$$

where $\mathbf{R} = (\mathbf{R}_1, \mathbf{R}_2)$. The $\varphi_i(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ form a complete set, so we can expand Ψ_s in terms of them:

$$\Psi_s(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2) = \sum_i \chi_i(\mathbf{R})\varphi_i(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}). \tag{14}$$

Plugging this into the Schrödinger equation for the whole system, we eventually arrive at a Schrödinger-like equation for the $\chi_i(\mathbf{R})$ (see the notes for details):

$$\left(T_\mathrm{p} + E_i(\mathbf{R})\right)\chi_i(\mathbf{R}) = E_{s,i}\chi_i(\mathbf{R}), \tag{15}$$

where E_s is the total system energy. We now change coordinates from $\{\mathbf{R}_1, \mathbf{R}_2\}$ to $\{\mathbf{R}_\mathrm{cm}, \mathbf{r}\}$, where $r \equiv |\mathbf{R}_1 - \mathbf{R}_2|$. The kinetic energy operator has a term for the center of mass and a term for the separation of the protons. The center of mass term has no potential and no rotation, and therefore contributes energy $\hbar^2k^2/2m$ to the total energy, which we'll set to zero. Its wave function will be a plane wave, $\chi_s^\mathrm{cm} = e^{i\mathbf{k}\cdot\mathbf{R}_\mathrm{cm}}/\sqrt{V}$. Now, we are interested in the rotational and the vibrational degrees of freedom. To solve this, we will separate the rotational and vibrational degrees of freedom, which we can do because the vibrational excitations are much higher energy than the rotational (the frequencies are of the order 10–1000 cm^{-1} and 1 cm^{-1}, respectively). In effect, this approximation treats the molecule as a *rigid rotor*, which means the atoms for the rotational problem as though they were fixed on the surface of a sphere of diameter $r \equiv |\mathbf{R}_1 - \mathbf{R}_2|$, which uncouples the vibrations and rotations and simplifies the problem considerably. The rigid rotor is described by two angles θ and ϕ. Then we consider small deviations of the separation from the equilibrium distance, which is simply a harmonic oscillator. Our equations for the vibrational and rotational degrees of freedom are therefore given by

$$\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + \frac{1}{2}kr^2\right)\chi_i^\mathbf{r} = E_{s,i}^r\chi_i^r \tag{16}$$

$$\frac{L^2}{2I}\chi_i^{\theta\phi} = -\frac{\hbar^2}{2\mu r^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\chi_i^{\theta\phi} = E_{s,i}^l\chi_i^{\theta\phi}, \tag{17}$$

where $\mu = m_p/2$ is the reduced mass. The rotational equation can further be separated into equations dependent only on θ and ϕ. The end result of this is (see any elementary quantum or electrodynamics text for the details) that $\chi_i^{\theta\phi} = Y_{lm}(\theta,\, \phi)$ and $E_s^l = l(l+1)/2\mu r^2$. The vibrational equation is simply that of a harmonic oscillator (because we made it that way). Its energies are $E_s^r = \hbar\omega(i + 1/2)$, and its solution is

$$\chi_i^r = \frac{1}{\sqrt{2^i i!}} \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\mu\omega}{2\hbar} r^2\right) H_i\left(\sqrt{\frac{\mu\omega}{\hbar}} r\right), \tag{18}$$

where the H_i are Hermite polynomials. Next, we will need the electronic wave functions. There is no exact solution, so let us simply write a generic antisymmetric wave function from the one-electron wave functions:

$$\varphi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\right) \tag{19}$$

Our overall wave function then takes the form

$$\chi_s^{ilm} = \chi_i^{\mathrm{cm}} \chi_i^r Y_{lm}(\theta,\, \phi)\varphi(\mathbf{r}_1, \mathbf{r}_2). \tag{20}$$

Finally, for our ground state solution, we set $i = l = m = 0$, and we have

$$\boxed{\begin{aligned}\chi_s^{000} = \sqrt{\frac{1}{4\pi}} \times \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{R}_{\mathrm{cm}}} \times \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\mu\omega}{2\hbar} r^2\right) \\ \times \frac{1}{\sqrt{2}} \left(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\right)\end{aligned}}$$

What about the first excited state? The difference in energy between states of a harmonic oscillator are $\hbar\omega = \hbar\sqrt{k/m}$. Unless the spring constant in our harmonic approximation is very large, this energy difference will be smaller than the energy differences in the electronic states. Furthermore, as discussed above, the rotational excitations are smaller than the vibrational excitations. Therefore, our first excited state will be $\Psi_s(\mathrm{ex.}) = \chi_0 Y_{1m}\varphi$:

$$\boxed{\begin{aligned}\chi_s^{01m} = \sqrt{\frac{3}{4\pi}} \cos\theta e^{im\phi} \times \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{R}_{\mathrm{cm}}} \times \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\mu\omega}{2\hbar} r^2\right) \\ \times \frac{1}{\sqrt{2}} \left(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\right)\end{aligned}}$$

Note that this state is triply degenerate because $m = \{-1,\, 0,\, 1\}$. The first excited vibrational state is simply $\Psi_s(\mathrm{ex.}) = \chi_1 Y_{00}\varphi$:

$$\boxed{\begin{aligned}\chi_s^{100} = \sqrt{\frac{1}{4\pi}} \times \frac{1}{\sqrt{V}} e^{i\mathbf{k}\cdot\mathbf{R}_{\mathrm{cm}}} \times \sqrt{\frac{1}{2}} \left(\frac{\mu\omega}{\pi\hbar}\right)^{1/4} \exp\left(-\frac{\mu\omega}{2\hbar} r^2\right) 2\sqrt{\frac{\mu\omega}{\hbar}} r \\ \times \frac{1}{\sqrt{2}} \left(\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) - \psi_2(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\right)\end{aligned}}$$

Problem 4

(a) Since we are working in a linear combination of atomic orbitals (LCAO) basis, our basis wave functions will be $|1\rangle$ and $|2\rangle$, which will be the $1s$ orbitals centered on atoms 1 and 2 respectively. Our Hamiltonian matrix in this basis will then be

$$\boxed{H_{ij} = \langle i \,|\, H \,|\, j \rangle} \tag{21}$$

(b) We set $\langle 1 \,|\, H \,|\, 1 \rangle = \langle 2 \,|\, H \,|\, 2 \rangle = \epsilon_0$ and $\langle 1 \,|\, H \,|\, 2 \rangle = -V$. The eigenvalues and (normalized) eigenvectors are then

$$\boxed{\begin{aligned} \epsilon_\pm &= \epsilon_0 \pm V \\ \psi_\pm &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \mp 1 \end{pmatrix} \end{aligned}} \tag{22}$$

(c) The lowest energy state will have both electrons in the bonding state (that we've labeled ψ_-). Note that the electrons will have opposite spins to satisfy the Pauli exclusion principle, even though we have not included spin in our Hamiltonian. Setting $\epsilon_0 = 0$ and $V = -2\,\text{eV}$, the total electronic energy is

$$\boxed{E_e = -2V = -4\,\text{eV}} \tag{23}$$

(d) We now let V depend on the separation of the atoms a d^{-2}, and we add a repulsive potential that goes as d^{-4} to prevent the molecule from collapsing. The total electronic energy is then

$$E_e = -\frac{2A}{d^2} + \frac{B}{d^4}. \tag{24}$$

Minimizing this with respect to d yields

$$d_0 = \sqrt{\frac{B}{A}} = 1\,\text{Å}, \tag{25}$$

where we have plugged in $A = 2\,\text{eV}\,\text{Å}^2$ and $B = 2\,\text{eV}\text{Å}^4$. A plot of the potentials is shown in Figure 2.

(e) We can minimize this numerically using Mathematica's built-in `NMinimize[]` function, which uses a simplex method. Doing so yields the same result as our analytic calculation:

$$\boxed{d_0 = 1.0\,\text{Å}} \tag{26}$$

(f) The Taylor expansion of the total energy is given by

$$E(d) \approx E(d_0) + \left.\frac{\partial E}{\partial d}\right|_{d=d_0} (d - d_0) + \left.\frac{\partial^2 E}{\partial d^2}\right|_{d=d_0} (d - d_0)^2. \tag{27}$$

The first derivative at d_0 vanishes (recall that requiring this was how we solved for d_0 to begin with). Plugging in for $E(d_0)$ and the second order term yields

$$E(d) \approx -\frac{A^2}{B} + \frac{8A^3}{B^2}(d - d_0)^2, \tag{28}$$

where, recall, that $d_0 = \sqrt{B/A}$. This is the harmonic approximation.

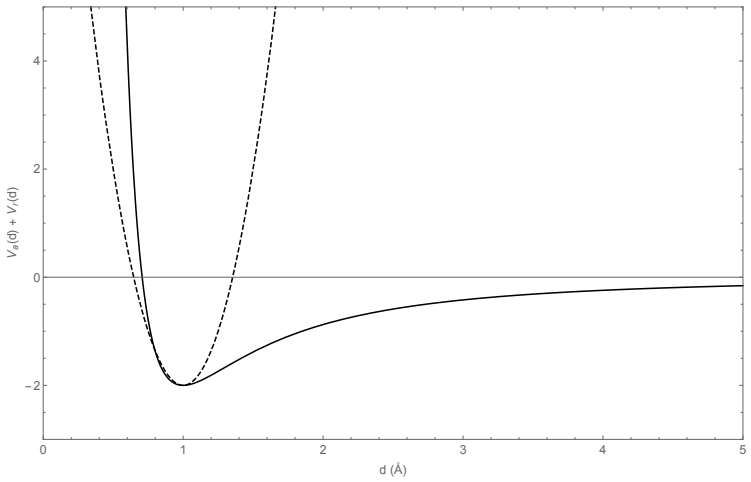

Figure 2: Plot of the attractive and repulsive potentials, exactly (solid line) and in the harmonic approximation (dashed line).

(g) If the energy expression governs the dimer dynamics, we can write the equation of motion as

$$M\ddot{x} = -Kx, \tag{29}$$

where K is the force constant (in general, this is a matrix, but this is a one-dimensional problem) and M is the reduced mass. The reduced mass is $M = m/2$, and we already calculated the force constant in the harmonic approximation above to be

$$K = \left.\frac{\partial^2 E}{\partial d^2}\right|_{d=d_0} = \frac{8A^3}{B^2}. \tag{30}$$

Recall that the angular frequency is given by

$$\omega = \sqrt{\frac{K}{M}} = \frac{4}{B}\sqrt{\frac{A^3}{m}}. \tag{31}$$

Plugging in for A, B, and m (make sure you have the correct units here!), we have

$$\boxed{\begin{aligned} \omega &= 5.553 \times 10^{14}\,\mathrm{rad\,s^{-1}} \\ f &= 8.838 \times 10^{13}\,\mathrm{Hz} \end{aligned}} \tag{32}$$

(h-j, k) The results of the numerical calculation are shown in Figures 3, 4, and 5. The Matlab code used to generate these results is included at the end of the solutions.

We can calculate the temperature from the velocity of our atoms. From the equipartition theorem, we can write the temperature in terms of the average square velocity as

$$T = \frac{m\bar{v}^2}{2k_B}. \tag{33}$$

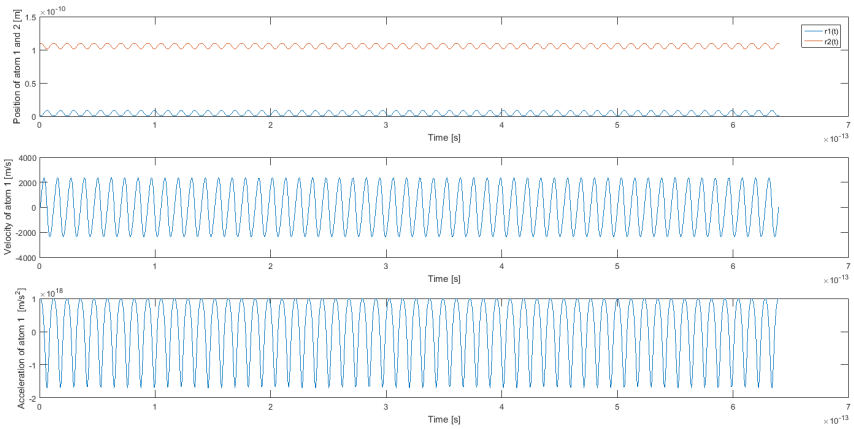

Figure 3: Position, velocity, and acceleration of one of the two atoms.

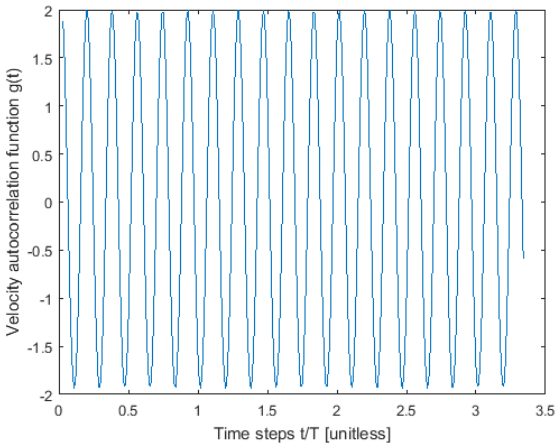

Figure 4: The velocity-velocity correlation function as a function of time.

(Note that since we have two hydrogen atoms, the total energy is $k_B T$.) Plugging in the mass of the hydrogen atom, Boltzmann's constant, and the average (RMS) velocity, we have

$$\boxed{T = 167.1\,\mathrm{K}} \tag{34}$$

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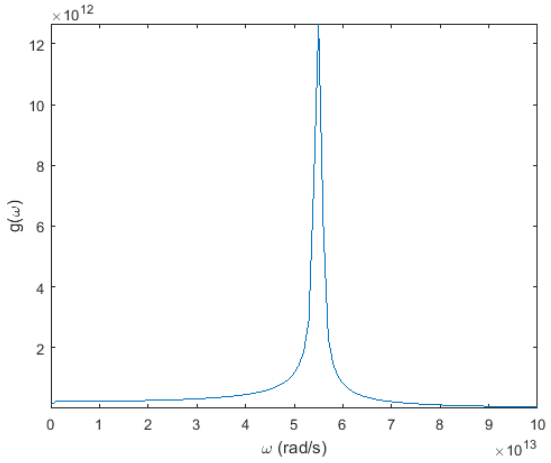

Figure 5: Bonus - the Fourier transform of the velocity-velocity correlation function.

Problem 5 (Bonus)

The Fock space is described by occupation numbers. The dimension of the Fock space therefore depends on the number of electrons and sites in the system. Our system has two sites. For no electrons then, the Fock space is 1 dimensional; for one electron, it is 4 dimensional; for two electrons, it is 6 dimensional, and so on.

For this system with two electrons, the possible basis kets are

$$\boxed{|\uparrow\uparrow\rangle\,,\ |\downarrow\downarrow\rangle\,,\ |\uparrow\downarrow\rangle\,,\ |\downarrow\uparrow\rangle\,,\ |\uparrow\downarrow\ \ 0\rangle\,,\ |0\ \ \uparrow\downarrow\rangle} \tag{35}$$

We can write this in the basis of the Fock space as

$$|1100\rangle\,,\ |1010\rangle\,,\ |1001\rangle\,,\ |0110\rangle\,,\ |0101\rangle\,,\ |0011\rangle\,. \tag{36}$$

To write $\langle x\,x'\,|\uparrow\downarrow\rangle$, first note that we can separate the spin and position wave functions. Because electrons are fermions and obey the Pauli exclusion principle, the total wave function must be antisymmetric. Finally, the product of an antisymmetric function and a symmetric function is antisymmetric, so we only need to antisymmetrize one of the wave functions. Doing so with the position wave function, we have

$$\boxed{\langle x\,x'\,|\uparrow\downarrow\rangle = \frac{1}{\sqrt{2}}\Big[\phi_a(x)\chi^+\phi_b(x')\chi^- - \phi_a(x')\chi^+\phi_b(x)\chi^-\Big]} \tag{37}$$

Matlab code for Problem 4

```
%%%%%%%%%%%%%%%%%%%%%%%% Definitions %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
A = 2 * 1.6 * (10^(-19))*(10^(-20)); % Is given for the potential
B = 2 * 1.6 * 10^(-19)*(10^(-40));  % Is given for the potential
mH = 1.67 * 10^(-27);               % Mass of one hydrogen
M = mH/2;                           % Reduced mass of hydrogen molecule
kB = 1.38064852e-23;
w = 9.81602*10^13;                   % Calculated frequency from part (g)
T = 2*pi/w;                         % Time needed for one period
dt = T/100;                         % Arbitrarily chosen time step of 100th of T
N = 1000;                           % Number of iterations
r1 = zeros(1,N);                    % Predefined position vector of atom 1
r2 = zeros(1,N);                    % Predefined position vector of atom 2
a1 = zeros(1,N);                    % Predefined acceleration vector of atom 1
a2 = zeros(1,N);                    % Predefined acceleration vector of atom 2
t = zeros(1,N);                     % Vector for my time steps, used for plotting
d = zeros(1,N);                     % Distance vector between atom 1 and 2
v1 = zeros(1,N);                    % Velocity vector of atom 1
v2 = zeros(1,N);                    % Velocity vector of atom 2

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% For the first time step dt we need to calculate the new ri(dt) and rj(dt) by hand:
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

r1(1,1) = 0*10^(-10);               % Initial position condition for atom 1
r2(1,1) = 2*10^(-10);              % Initial position condition for atom 2
v0 = 0;                             % Initial velocity, will be assigned to both
    atoms
v1(1,1) = v0;                       % Initial velcoity of atom 1
v2(1,1) = v0;                       % Initial velocity of atom 2
t(1,1) = dt;                        % Initialization of the time vector going in
    increments of dt
t(1,2) = 2*dt;

d(1,1) = abs(r2(1,1)-r1(1,1));     % Calculates the initial distance using the
    initial position conditions
% Calculation of the initial accelerations for the first time step
a1(1,1) = 1/mH *(r1(1,1)-r2(1,1))*(4*B/d(1,1)^6 - 4*A/d(1,1)^4);
a2(1,1) = -1/mH *(r1(1,1)-r2(1,1))*(4*B/d(1,1)^6 - 4*A/d(1,1)^4);

% Using our calculated accelerations, we can find the new positions after
% the time step dt.
r1(1,2) = r1(1,1) + dt*v0 + (dt^2/2)*a1(1,1);
r2(1,2) = r2(1,1) + dt*v0 + (dt^2/2)*a2(1,1);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
% After the first values are calculated, we can use an algorithm to find
```

```
% the remaining values for the acceleration, position and velocity
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
for i = 3:N

    d(1,i-1) = abs(r1(1,i-1) - r2(1,i-1));
    a1(1,i-1) = 1/mH *(r1(1,i-1)-r2(1,i-1))*(4*B/d(1,i-1)^6 - 4*A/d(1,i-1)^4);
    a2(1,i-1) = -1/mH *(r1(1,i-1)-r2(1,i-1))*(4*B/d(1,i-1)^6 - 4*A/d(1,i-1)^4);

    r1(1,i) = 2*r1(1,i-1) - r1(1,i-2) + (dt)^2*a1(1,i-1);
    r2(1,i) = 2*r2(1,i-1) - r2(1,i-2) + (dt)^2*a2(1,i-1);

    t(1,i) = i*dt;
    v1(1,i-1) = (r1(1,i)-r1(1,i-2))/(2*dt);
    v2(1,i-1) = (r2(1,i)-r2(1,i-2))/(2*dt);
end
d(1,N) = abs(r1(1,N) - r2(1,N));
a1(1,N) = 1/mH *(r1(1,N)-r2(1,N))*(4*B/d(1,N)^6 - 4*A/d(1,N)^4);
a2(1,N) = -1/mH *(r1(1,N)-r2(1,N))*(4*B/d(1,N)^6 - 4*A/d(1,N)^4);


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%% Plots of the result %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
figure;
subplot(3,1,1)
plot(t,r1,t,r2)
xlabel('Time [s]')
ylabel('Position of atom 1 and 2 [m]')
legend('r1(t)', 'r2(t)');

subplot(3,1,2)
plot(t(1,1:N-1),v1(1,1:N-1))
xlabel('Time [s]')
ylabel('Velocity of atom 1 [m/s]')

subplot(3,1,3)
plot(t,a1)
xlabel('Time [s]')
ylabel('Acceleration of atom 1 [m/s^2]')


%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%% CALCULATION OF THE AUTOCORELLATION FUNCTION %%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%


j = 2;                          % Because we used the initial velcocity condition v0
    = 0, which is assigned to the vector position v1(1,1), we start at v1(1,2),
    which is a non-zero velocity, so j=2 defines our arbitrarily chosen starting
```

```
    point t0.
tau = N-j;                      % Since t= tau*dt, this calculates the total number
    of taus possible until we reach the maximum time, which is defined by dt and the
    number of iterations
sum1 = zeros(tau-1,1);          % Calculates the sum of the numerator of atom 1 of
    the autocorrelation function
sum2 = zeros(tau-1,1);          % Calculates the sum of the numerator of atom 2 of
    the autocorrelation function
Denom1 = zeros(tau-1,1);        % Calculates the Denominator of atom 1 of the
    autocorelation function
Denom2 = zeros(tau-1,1);        % Calculates the Denominator of atom 2 of the
    autocorelation function
t = t'/T;                       % Time as a fraction of T, looks better for plots
    this way

%%%%%%%%%%%%% Calculation of the numerator sums %%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

for x = 1:tau-1
    for i = j:N
        if i+x <= N-1
            sum1(x,1) = sum1(x,1) + v1(1,i+x)*v1(1,i);   % Adds v1(t0+tau)*v1(t0) to
                the previously calculated value
            sum2(x,1) = sum2(x,1) + v2(1,i+x)*v2(1,i);   % Adds v2(t0+tau)*v2(t0) to
                the previously calculated value
        else
            break;
        end
    end
    sum1(x,1) = 1/(N-x-j) * sum1(x,1);      % Divides the calculated sum by the
        number of terms to get the average
    sum2(x,1) = 1/(N-x-j) * sum2(x,1);      % Divides the calculated sum by the
        number of terms to get the average
end


%%%%%%%%%%%%%%%%%%%% Calculation of Denominators %%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

for x = 1:tau-1
    for i = j:N-1
     Denom1(x,1) = Denom1(x,1) + v1(1,i).^2;    % Adds v1(t0)*v1(t0) to the
         previously calculated term
     Denom2(x,1) = Denom2(x,1) + v2(1,i).^2;    % Adds v2(t0)*v2(t0) to the
         previously calculated term
    end
    Denom1(x,1) = 1/(N-j) * Denom1(x,1);        % Divides the calculated sum by the
        number of terms to get the average
    Denom2(x,1) = 1/(N-j) * Denom2(x,1);        % Divides the calculated sum by the
        number of terms to get the average
```

```
end


p = sum1./Denom1 + sum2./Denom2;           % Calculates the correlation function
g = p(1:tau-1);                            % Because our velocities are only defined
    for N-1, we only use tau-1 values.

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%% Plots of the result %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
figure;
plot(t(j+1:334,1),g(1:332,1));
xlabel('Time steps t/T [unitless]')
ylabel('Velocity autocorrelation function g(t)')



%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%% CALCULATION OF THE FOURIER TRANSFORM %%%%%%%%%%%%%%%%%%%%%%%%
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

W = zeros(N-j-1,1);   % Calculates each point of the W(t) function under the integral

% Calculation of W(t) and the cosine for each time step dt
for i = 1:N-1-j
    W(i,1) = 0.42-0.5*cos(pi*i*dt/(N*dt)) + 0.08*cos(2*pi*i*dt/(N*dt));
end

t = t*T;

L = N;                % Sampling length
Fs = 1e15;            % Sampling frequency
T1 = 1/Fs;

f = 1/T*(g.*W); % Function to use to perform the FFT
F = fft(f);           % Fast Fourier Transform of our function f

figure;
P2 = abs(F/L);
P1 = P2(1:L/2+1);     % We are only interested in the first half of the calculated
    values
P1(2:end-1) = 2*P1(2:end-1); % The first number is the constant a0 so we start
    plotting from the vector component
freq = Fs*(0:(L/2))/L; % Frequency for plotting
plot(freq,P1);        % Plots the FFT vs frequency
xlabel('\omega (rad/s)')
ylabel('g(\omega)')
axis([0,1e14, -inf, inf]);

temperature = 0.5*(mean(v1.^2)*mH/kB ) %#ok<NOPTS>
```