Problem 4

The classical Hamiltonian for a diatomic molecule AB is

$$H = \frac{p_A^2}{2m_A} + \frac{p_B^2}{2m_B} + V(|R_A - R_B|)$$

where $R_{A,B}$ are the positions of the two nuclei and $P_{A,B}$ the conjugate momenta. We have expressed the potential in the above equation in terms of the distance $|R_A - R_B| \equiv r$ between the two atoms, assuming that there are no external fields acting on the system. Perform a canonical transformation to new coordinates $R$ and $r$, where $R$ is the center-of-mass coordinate,

$$R = \frac{m_AR_A + m_BR_B}{m_A + m_B}$$

and $r = R_A - R_B$, and show that the Hamiltonian can be expressed in terms of these new coordinates in the form

$$H = \frac{p_R^2}{2M} + \frac{p_r^2}{2\mu} + V(r)$$

where $M = m_A + m_B$, $\mu = m_A m_B / M$, and $P_R$, $P_r$ are the momenta conjugate to $R$ and $r$, respectively. The first term in the new Hamiltonian corresponds to the kinetic energy of the center of mass of the molecule and represents rigid translation in space, while the part depending on $r$ describes rotation and vibration.