

Theory

Basis

We utilise a complete basis of the form, $\mathcal{B} = \{|\phi_i\rangle\}_{i=1}^N$, where the basis functions are represented in coordinate-space in the form

$$\phi_i(r, \Omega) = \frac{1}{r} \varphi_{k_i, \ell_i}(r) Y_{\ell_i}^{m_i}(\Omega) \quad \text{for } i = 1, \dots, N \quad (1)$$

where the radial functions, $\mathcal{R} = \{|\varphi_{k_i, \ell_i}\rangle\}_{i=1}^N$ form a complete basis for the radial function space, in the limit as $N \rightarrow \infty$. We utilise a Laguerre basis for the set of radial functions which, for $k = 1, 2, \dots$ and where $\ell \in \{0, 1, \dots\}$, are of the following form in coordinate-space

$$\varphi_{k, \ell}(r) = N_{k, \ell} (2\alpha_\ell r)^{\ell+1} \exp(-\alpha_\ell r) L_{k-1}^{2\ell+1}(2\alpha_\ell r) \quad (2)$$

where $\alpha_\ell \in (0, \infty)$ are arbitrarily chosen constants, where $N_{k, \ell}$ are the normalisation constants, given by

$$N_{k, \ell} = \sqrt{\frac{\alpha_\ell (k-1)!}{(k+\ell)(k+2\ell)!}} \quad (3)$$

and where $L_{k-1}^{2\ell+1}$ are the generalised Laguerre polynomials.

Overlap Matrix Elements

The overlap matrix elements, $B_{i,j}$, are of the form

$$B_{i,j} = \langle \phi_i | \phi_j \rangle = \langle \frac{1}{r} \varphi_{k_i, \ell_i} | \frac{1}{r} \varphi_{k_j, \ell_j} \rangle \langle Y_{\ell_i}^{m_i} | Y_{\ell_j}^{m_j} \rangle = \langle \frac{1}{r} \varphi_{k_i, \ell_i} | \frac{1}{r} \varphi_{k_j, \ell_j} \rangle \delta_{\ell_i, \ell_j} \delta_{m_i, m_j} \quad (4)$$

where

$$\langle \frac{1}{r} \varphi_{k_i, \ell_i} | \frac{1}{r} \varphi_{k_j, \ell_j} \rangle = \begin{cases} 1, & \text{if } k_i = k_j \\ -\frac{1}{2} \sqrt{1 - \frac{\ell(\ell+1)}{(k_i + \ell)(k_i + \ell + 1)}}, & \text{if } k_j = k_i + 1 \\ \langle \frac{1}{r} \varphi_{k_j, \ell_j} | \frac{1}{r} \varphi_{k_i, \ell_i} \rangle, & \text{if } k_i = k_j + 1 \\ 0, & \text{otherwise} \end{cases} \quad (5)$$

Kinetic Matrix Elements

The kinetic matrix elements, $K_{i,j}$, are of the form

$$K_{i,j} = \langle \phi_i | \hat{K} | \phi_j \rangle = \alpha^2 (\delta_{k_i, k_j} - \frac{1}{2} \langle \frac{1}{r} \varphi_{k_i, \ell_i} | \frac{1}{r} \varphi_{k_j, \ell_j} \rangle) \delta_{\ell_i, \ell_j} \delta_{m_i, m_j}. \quad (6)$$

Spherically-Symmetric Potential Matrix Elements

For a spherically symmetric potential, $V(r, \Omega) = V(r)$, the potential matrix elements can be calculated numerically to be of the form

$$V_{i,j} = \langle \phi_i | \hat{V} | \phi_j \rangle = \langle \frac{1}{r} \varphi_{k_i, \ell_i} | \hat{V} | \frac{1}{r} \varphi_{k_j, \ell_j} \rangle \delta_{\ell_i, \ell_j} \delta_{m_i, m_j} \quad (7)$$

where

$$\langle \frac{1}{r} \varphi_{k_i, \ell_i} | \hat{V} | \frac{1}{r} \varphi_{k_j, \ell_j} \rangle = \int_0^\infty dr \varphi_{k_i, \ell_i}(r) V(r) \varphi_{k_j, \ell_j}(r). \quad (8)$$

1 H_2^+ Potential-Energy Curves

Details of Relevant Theory and Code

Axially-Symmetric Potential

The axially-symmetric potential of the H_2^+ molecule, with two nuclei at $\mathbf{R} = (0, 0, \pm \frac{R}{2})$, can be written in the form

$$V(r, \Omega) = - \left(\frac{1}{\|\mathbf{r} + \mathbf{R}\|} + \frac{1}{\|\mathbf{r} - \mathbf{R}\|} \right) \quad (9)$$

which can be written alternatively, using the multipole expansion, in the form

$$V(r, \Omega) = -2 \sum_{\lambda \in E} \sqrt{\frac{4\pi}{2\lambda + 1}} \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} Y_\lambda^0(\Omega) \quad (10)$$

where $r_{<} = \min(r, \frac{R}{2})$, $r_{>} = \max(r, \frac{R}{2})$, and where $E = \{0, 2, 4, \dots\}$ is the set of even integers. Note that in computational implementations, we truncate this sum at some term, λ_{\max} . Whence, it follows that the matrix elements for this potential can be calculated numerically to be of the form

$$V_{i,j} = \langle \phi_i | \hat{V} | \phi_j \rangle = -2 \sum_{\lambda \in E} \left(\int_0^\infty dr \varphi_{k_i, \ell_i}(r) \frac{r_{<}^\lambda}{r_{>}^{\lambda+1}} \varphi_{k_j, \ell_j}(r) \right) \left(\sqrt{\frac{4\pi}{2\lambda + 1}} \langle Y_{\ell_i}^{m_i} | Y_\lambda^0(\Omega) | Y_{\ell_j}^{m_j} \rangle \right) \times \delta_{\pi_i, \pi_j} \delta_{m_i, m_j} \quad (11)$$

where $\pi_i = (-1)^{\ell_i}$ is the parity quantum number.

Basis Symmetry

Due to the axial symmetry of the H_2^+ potential, and thus the Hamiltonian for the electron in this molecule, we may choose a symmetrised basis $\mathcal{B}^{(m, \pi)}$ with specified azimuthal angular momentum, m , and parity, π . Furthermore, due to the computational constraints, we restrict our basis to having $\{N_\ell\}_{\ell=0}^{\ell_{\max}}$ radial functions per ℓ , with exponential falloffs $\{\alpha_\ell\}_{\ell=0}^{\ell_{\max}}$. For simplicity, we select $N_\ell = N_0$, and $\alpha_\ell = \alpha_0$, for each $\ell = 0, \dots, \ell_{\max}$.

1.1 Comparison with Accurate Potential-Energy Curve for $1s\sigma_g$.

1.2 Comparison with Accurate Potential-Energy Curve for $2p\sigma_u$.

2 H_2^+ Vibrational Wave Functions

Details of Relevant Theory and Code

2.1 Vibrational Wave Functions for $1s\sigma_g$ PEC.

2.2 Lowest-Energy, $\nu = 0$, Vibrational Wave Functions for $1s\sigma_g$ PEC, for each Isotopologue of H_2^+ .