Ab initio Calculation of the Potential Energy Curve of H_2

Introduction

The hydrogen molecule (H_2) is the simplest polyelectronic molecular system, involving only 2 nuclei and 2 electrons. This makes it the best place to start learning about how theoretical molecular energy calculations can be performed. For more complex systems, molecular energy calculations require a large number of electron wavefunctions and significant amounts of computing power to create a good approximation to the true molecular wavefunction. However, performing qualitatively good calculations on H_2 is possible on an ordinary laptop, although the mathematical calculations are still fairly involved. As such, my project over the course of the UTRIP program was to derive the potential energy curve of H_2 from first principles.

Basis Set

The spatial atomic orbitals of a hydrogen atom are known exactly, and they have the form $\varphi(\underline{r}) = \exp[-a|\underline{r}-\underline{R}|]$, where $\underline{r}$ is the position vector of the electron and $\underline{R}$ the position of the hydrogen nucleus. However, functions of this type (Slater orbitals) are mathematically difficult to manipulate, so it is common to use functions of Gaussian form, $\varphi(\underline{r}) = \exp[-a(\underline{r}-\underline{R})^2]$. As a result, one Gaussian type orbital on each hydrogen atom was taken as the basis set in this approximation. Although this is a tiny basis set and a poor approximation to the real orbitals, it is not only good enough to give an initial insight into how molecular energies can be calculated, but also to give a qualitatively adequate potential energy curve.

Molecular Wavefunction

Due to the high mass ratio between electrons and nuclei, it is a good approximation to assume that the nuclei are fixed relative to the electronic movement (Born-Oppenheimer approximation), so this was done to calculate the energy at various internuclear distances. For the overall electronic wavefunction, a Slater determinant of 1-electron orbitals was used in order to satisfy the Pauli Principle that the wavefunction must be antisymmetric with respect to electron exchange. This gives the electronic wavefunction as:

$$\Psi = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi(1)\alpha(1) & \psi(1)\beta(1) \\ \psi(2)\alpha(2) & \psi(2)\beta(2) \end{vmatrix}$$

The one electron spatial orbitals, $\psi(i)$, are linear combinations of the spatial atomic orbitals given above, so $\psi = N\{\exp[-a(\underline{r}-\underline{R_A})^2] + \exp[-a(\underline{r}-\underline{R_B})^2]\}$ where N is the normalisation constant and $\underline{R_I}$ is the position of nucleus I. This linear combination is good near the equilibrium bond length. However, in the dissociation limit it predicts that each electron will still spend equal time on each H atom, when in reality each electron becomes localised onto one nucleus. This causes some problems with energy calculations in the dissociation limit.

Molecular Integral Calculation

The main body of this task involved the calculation of molecular integrals. Although computer programs are available to do these quickly for Gaussian type orbitals, it was decided that for a first molecular energy calculation it would be instructive to perform the integrals by hand, to understand how they are solved and also to gain an appreciation of the need for computer programs to solve them more efficiently.

Molecular integrals arise because the energy of the system is given by $\langle\Psi|\hat{H}|\Psi\rangle$. When the expression for Ψ in terms of atomic orbitals is substituted in, and the 7 terms of the Hamiltonian (4 electron-nuclear attractions, 2 electron kinetic energies and 1 electron-electron repulsion term) are considered, this expands to give 448 separate energy integrals, even for this very simple system. Fortunately, half of these are 0 due to spin orthogonality, and many of the other integrals are also equal due to the symmetry of the wavefunction, meaning there are in fact many fewer integrals to

calculate.

These energy integrals fall into 3 categories depending on which part of the Hamiltonian they arise from. These categories are kinetic energy integrals (of the form $\langle i|-d^2/d\underline{r}^2|j\rangle$), electron-nucleus attraction integrals (of the form $\langle i|-1/(\underline{r}-\underline{R}_K)|j\rangle$) and electron-electron repulsion integrals (of the form $\langle ij|1/(\underline{r}_1-\underline{r}_2)|kl\rangle$).

Calculating the Total Energy

The total electronic energy of the system is given by summing these molecular integrals (after multiplying by the correct coefficients). However, to obtain the total energy, the internuclear repulsion (which is $1/[\underline{R}_A-\underline{R}_B]$) must also be added. Also, the true energy of 2 free H atoms has been subtracted, in order to obtain the binding energy of the approximate wavefunctions. This means that the energy should tend to 0 as the bond length increases.

To find the molecular energy at a large number of internuclear distances it made sense to create a computer program to do many calculations quickly. This could also be used to optimise the exponential coefficients in the wavefunction, to obtain the best possible energy – optimisation of the atomic orbitals leads to a value of $a=0.26au^{-2}$ in the Gaussian exponentials, and this is the value used throughout this text. As H_2 is a homonuclear diatomic, the symmetry of the system means it is not necessary to perform any self-consistent field calculations, making the calculations of the potential energy curve very rapid.

Results

As explained above, the electronic energy of the system can be split into 3 categories with definite classical analogues. Below is a graph of each of these, as calculated by the Fortran computer code:
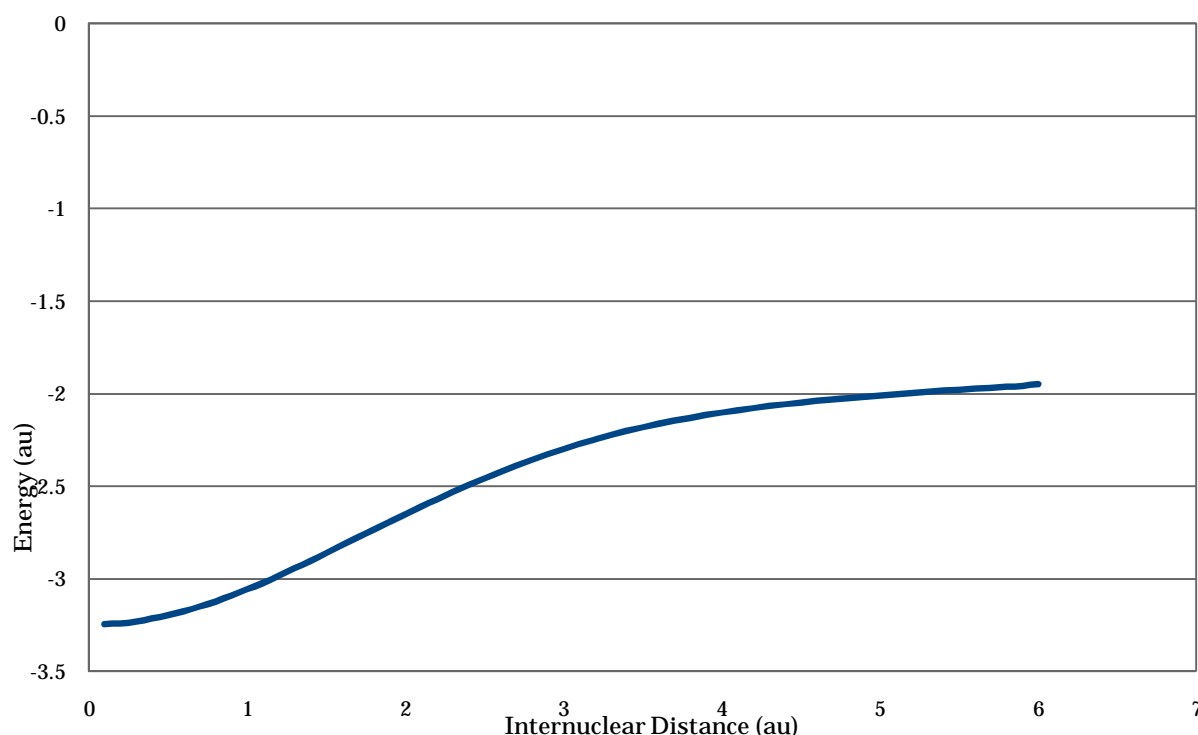

Fig. 1. Electron-nucleus attraction energy in H_2 as a function of internuclear distance ($a=0.26au^{-2}$)

The attraction of the electrons for the nucleus is the most significant term for binding in the molecule. In fact, it is the only negative term in this approximation, so is solely responsible for bonding. From Fig. 1 it can be seen that as the nuclei get further apart the attraction energy becomes less negative. This is because at large internuclear distances an electron will only ever be close to one nucleus. However, when the nuclei are close together an electron can be close to both nuclei

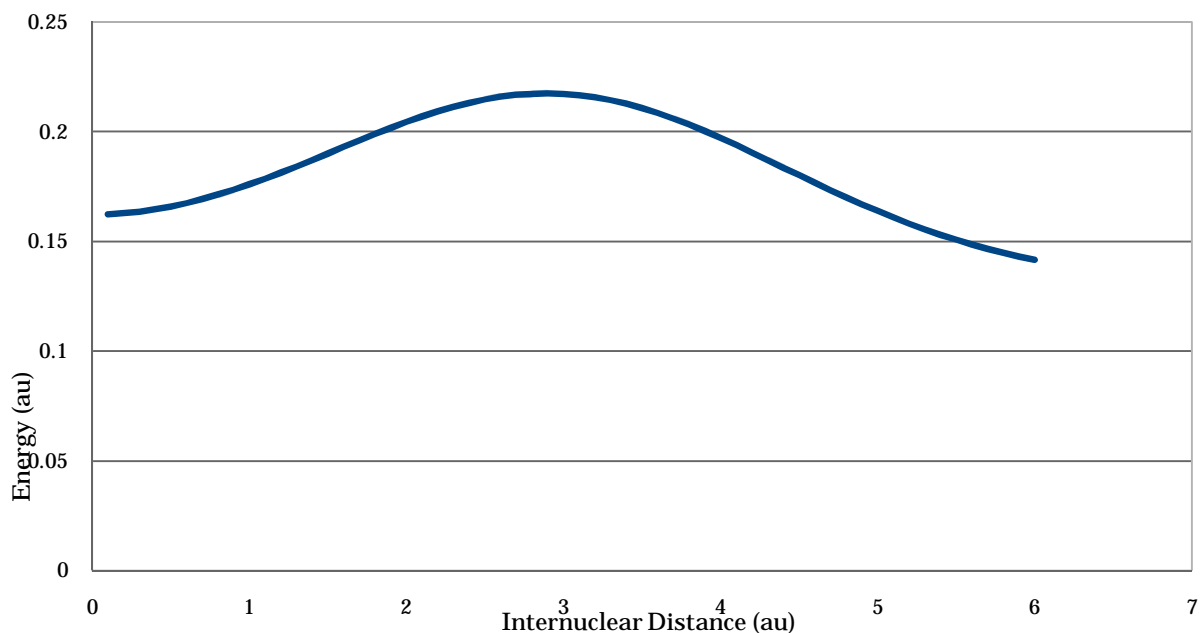simultaneously, lowering the energy of the system at these distances.

Fig. 2. Electron kinetic energy in H_2 as a function of internuclear distance (a=0.26au^{-2})

Electron kinetic energy is closely related to the size of the orbital it is in, as kinetic energy is given by the second spatial derivative which will generally decrease as the orbital size increases. As a result, we expect the kinetic energy to increase with internuclear distance as the electrons become localised onto one atom, rather than being spread over both. From Fig. 2 we can see that this is not true in this case. This is because the wavefunction that has been used is incorrect in the dissociation limit as it assumes that the electrons are always equally likely to be located on each hydrogen. This results in the electron orbitals increasing in size as the bond length increases, rather than decreasing as we would expect.
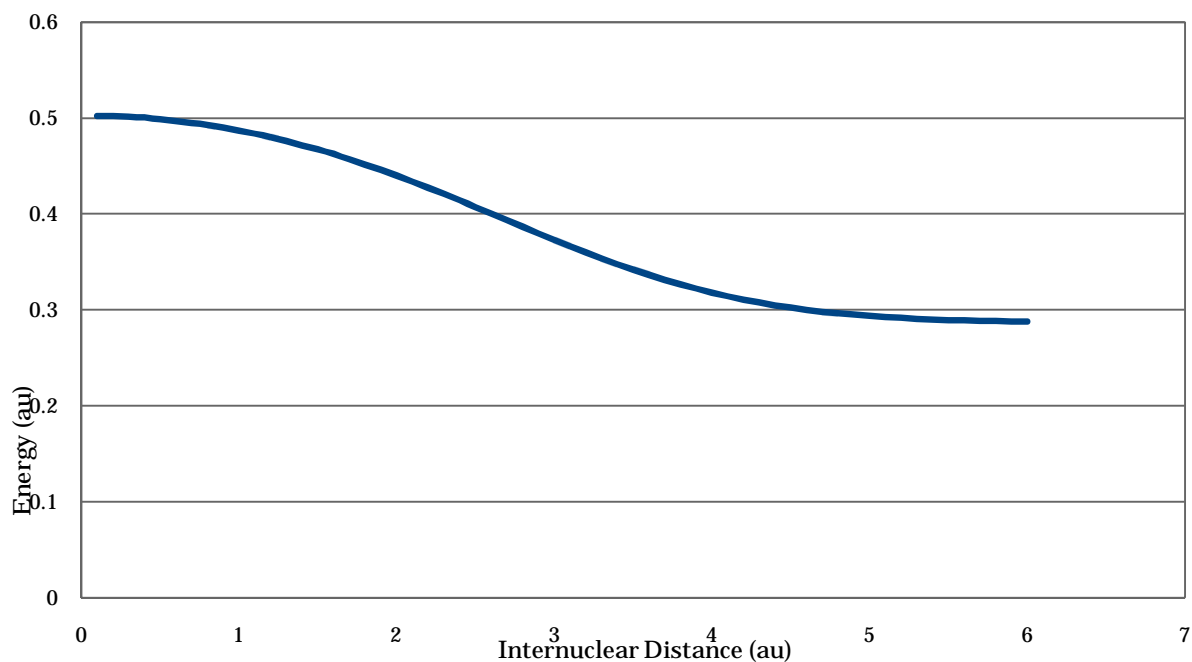

Fig. 3. Electron-electron repulsion energy in H_2 as a function of internuclear distance (a=0.26au^{-2})

The electron-electron repulsion is related to the internuclear distance, as the increasing distance between nuclei means the electrons will on average be further apart. In reality, however, the electron-electron repulsion should tend to 0 at large internuclear distances as the electrons will be localised on separate nuclei at a far distance. This doesn't occur with the simple wavefunction used here, as there is a finite probability of the electrons being on the same hydrogen, even at infinite bond length. This means that about half the electron-electron repulsion remains in this limit.
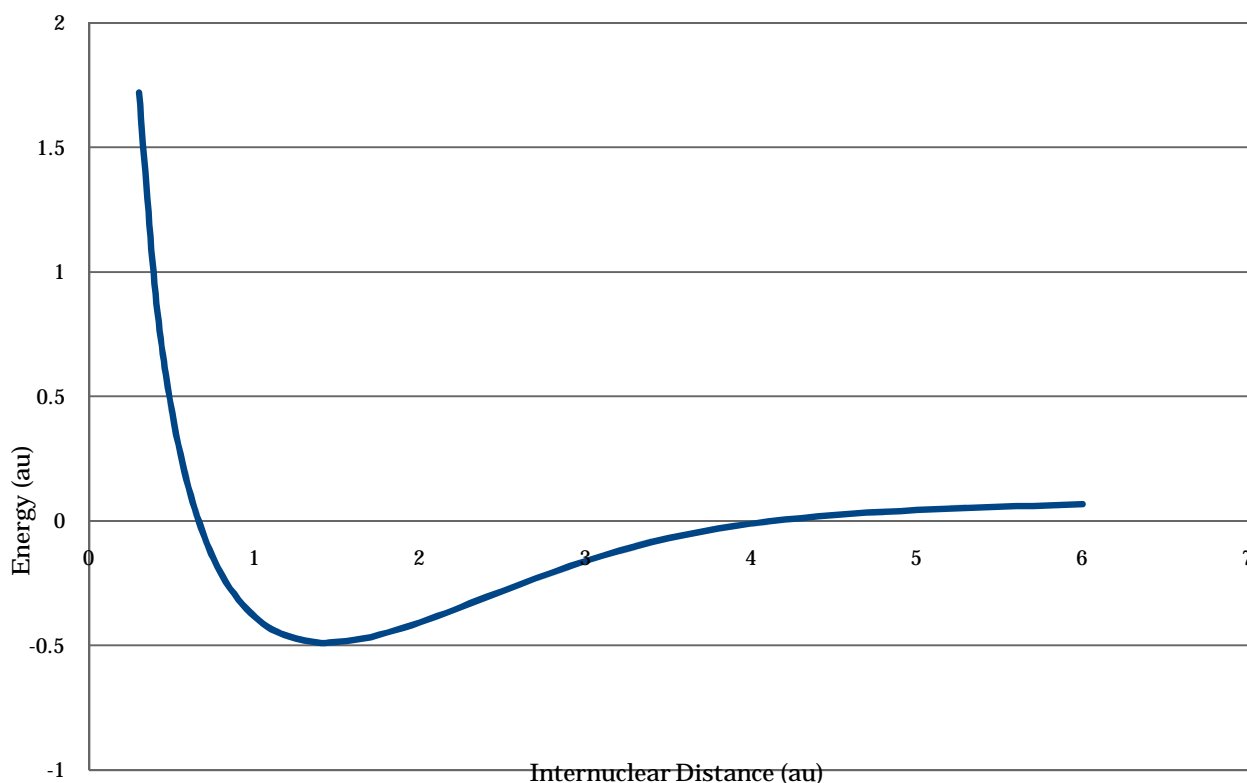

Fig. 4. The potential energy curve of H_2 as calculated using the simple model described in the main text (a=0.26au^{-2})

The calculated potential energy curve of H_2 is in good qualitative agreement with the true curve – there is a lot of repulsion at very short distances as the nuclear repulsion becomes large, there is a bound region where the total energy is less than 0 (meaning H_2 is a stable molecule) and the energy tends to a constant value at large bond lengths. Also, there is even good quantitative agreement of the calculated bond length with experimental data – the energy minimum occurs at a bond length of 1.388 au compared with the actual equilibrium bond length of 1.401 au.

The value of the energy is less good – the calculated value is only 45% of the true value. However, this is to be expected given the simplicity of the basis set used to create this model.

Improvements

As the wavefunction that has been used is so simple there are obviously some significant improvements that can be made.

Firstly, the atomic orbital basis set that has been used could be improved. There are two main ways this could be done – firstly, the exact Slater orbitals, with optimised coefficients, could be used to calculate a good approximation. However, it will be computationally much more difficult to use Slater orbitals, so a better approach may be to use a linear combination of Gaussian functions as the atomic orbitals, to more closely approximate the Slater-type orbital. In general, a combination of 3 Gaussian functions is a good approximation, although occasionally more are used.

Another improvement would be to solve the problems that arise in the dissociation limit. This could be achieved by including a variable in the 1-electron wavefunctions to allow for the localisation of

the electrons onto one hydrogen each at dissociation. For example, we set $\psi = N\{\exp[-a(\underline{r}-\underline{R_A})^2] + \zeta\exp[-a(\underline{r}-\underline{R_B})^2]\}$ where ζ is a function of bond length (tending to 0 or ∞ at large bond lengths)

Inclusion of other orbitals (2s, 2p, etc.) will slightly improve the energy we calculate, but the effect of this will be minimal as there is such a large energy gap between the 1s and 2s orbitals of hydrogen.

Conclusion

Although the energy calculated is significantly wrong, the techniques used to calculate it can be applied to much more complicated systems, using more accurate wavefunctions to represent the electrons. Also, even though the approximation to the wavefunctions was so simple, it was still good enough to be in qualitative agreement with the experimental results, meaning there may be situations where using a model this simple is appropriate in order to gain a basic insight into complex problems.