Using a Spreadsheet to Solve the Schrödinger Equations for H$_2$ in the Ground and Excited States

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“I think you should be more explicit here in Step Two.”
By Sidney Harris, Copyright 2007, The New Yorker
Goals

Better understanding of quantum chemistry

- by visualizing quantum phenomena on a spreadsheet
- by solving Schrödinger equation for molecules by hand
- by breaking the total energy into pieces
  - Kinetic energy of each electron.
- by hand calculating exchange and correlation energy on a spreadsheet.
Prior Knowledge

- Multivariable differential and integral calculus
- Quantum mechanical postulates:
  \[ \hat{\mathcal{H}} \psi = \varnothing \psi \]
  \[ \langle \mathcal{O} \rangle = \frac{\int \psi \hat{\mathcal{O}} \psi d\tau}{\int \psi \psi d\tau} \text{ (when } \psi \text{ is a real function.)} \]
- Linear algebra and differential equations are not required
- Experience with Excel or Google spreadsheet
Quantum chemistry exercises on a spreadsheet

- Ex. 1. Visualization of tunneling effect in a H atom
- Ex. 2. Visualization of particle-like properties of waves
- Ex. 3. Solving the Schrödinger equation for H$_2^+$ and H$_2$
- Ex. 4. Exchange energy in H$_2^*$: first singlet vs triplet excited states
- Ex. 5. Correlation energy in H$_2$: a 2-determinant wave function
Ex. 1. Visualization of tunneling effect in a H atom

\[ \frac{-1}{2} \nabla^2 \psi - \frac{1}{r} \psi = E \psi \]

Students can verify that \( \psi = e^{-r} \) is an eigenfunction with \( E = -\frac{1}{2} \) au.

<table>
<thead>
<tr>
<th>Radius (r)</th>
<th>Total E</th>
<th>Potential E</th>
<th>Kinetic E</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>4</td>
<td>-0.5</td>
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</tr>
</tbody>
</table>

… … … … …
Ex. 2. Visualization of particle-like properties of waves

Double-slit diffraction patterns of electrons visually illustrate the wave-like properties of particles.
Ex. 2. Visualization of particle-like properties of waves

Photoelectric effects illustrate (less visually) the particle-like property of light.
Ex. 2. Visualization of particle-like properties of waves

Visualization of the particle-like property of waves on a spreadsheet:

\[ \Psi = \frac{\cos(\theta) + \cos(2\theta) + \cos(3\theta) + \cos(4\theta)}{4} \]

<table>
<thead>
<tr>
<th>θ</th>
<th>cos(θ)</th>
<th>cos(2θ)</th>
<th>cos(3θ)</th>
<th>cos(4θ)</th>
<th>Ψ</th>
<th>Ψ²</th>
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<td>0.96</td>
<td>-0.91</td>
<td>0.84</td>
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<td>0.00</td>
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<td>0.84</td>
<td>-0.02</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Combination of many waves exhibit particle-like property

\[ \Psi = \sum_{n=1}^{N} \frac{\cos(n\theta)}{N} \]

- $N = 1$
- $N = 10$
- $N = 100$

Number of values the momentum ($p = \hbar/\lambda$) may have:
- $1$
- $10$
- $100$

Uncertainty of position

Uncertainty of momentum
Ex. 3. Solving the Schrödinger equation for $H_2^+$ and $H_2$

- Introduction to solving problems without analytical solutions.
- Nucleus positions fixed with a bond length of 1.5 a.u.
- Calculate every potential and kinetic energy component approximately.
- Need to evaluate integrals on a spreadsheet.
Integral calculation on a spreadsheet

• Using a spreadsheet to estimate the value of an integral:

\[ \int_{-L}^{L} f(x) \, dx \approx \sum_{i=-L}^{L} f(i) \]

• For a fast decaying function \( f(x,y,z) \), the function value at several thousand randomly selected data points are calculated within a given volume.

• The product of the volume and the average function value is approximately the integral.
\[
\int_{-\infty}^{\infty} \Psi \hat{O} \Psi d\tau \approx V \frac{\sum_{i=1}^{N} \Psi(\tau_i) \hat{O} \Psi(\tau_i)}{N}
\]
$- \frac{1}{2} \nabla^2 (e^{-r}) = (\frac{1}{r} - \frac{1}{2}) e^{-r}$

<table>
<thead>
<tr>
<th>$e^{-r_A}$</th>
<th>$e^{-r_B}$</th>
<th>$\phi_A + \phi_B$</th>
<th>Attraction</th>
<th>Kinetic E</th>
</tr>
</thead>
<tbody>
<tr>
<td>x</td>
<td>y</td>
<td>z</td>
<td>$r_A$</td>
<td>$r_B$</td>
</tr>
<tr>
<td>0.3</td>
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<td>-2.4</td>
<td>1.5</td>
<td>2.4</td>
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<tr>
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<td>1.7</td>
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<td>2.4</td>
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<td>1.0</td>
<td>1.4</td>
<td>1.9</td>
<td>1.9</td>
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<td>2.2</td>
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<td>-1.6</td>
<td>0.8</td>
<td>1.9</td>
<td>1.9</td>
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<td>3.1</td>
<td>3.1</td>
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<td>1.2</td>
<td>-0.7</td>
<td>2.0</td>
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<td>0.0</td>
<td>-1.2</td>
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<tr>
<td>...</td>
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</tbody>
</table>
Nucleus positions fixed with a bond length of 1.5 a.u.
No exchange energy between electrons with opposite spin.
Hartree product wave function $\psi = \sigma(1)\sigma(2)$ is used.
There are more columns but calculations can still be done conveniently on a spreadsheet.

<table>
<thead>
<tr>
<th>x₁</th>
<th>y₁</th>
<th>z₁</th>
<th>x₂</th>
<th>y₂</th>
<th>z₂</th>
<th>r₁A</th>
<th>r₁B</th>
<th>r₂A</th>
<th>r₂B</th>
<th>r₁2</th>
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</thead>
<tbody>
<tr>
<td>...</td>
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<td>...</td>
<td>...</td>
<td>...</td>
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<td>...</td>
<td>...</td>
<td>...</td>
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</tbody>
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<table>
<thead>
<tr>
<th>φ₁A</th>
<th>φ₁B</th>
<th>φ₂A</th>
<th>φ₂B</th>
<th>σ₁</th>
<th>σ₂</th>
<th>ψ</th>
<th>σ₁σ₂</th>
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<td>...</td>
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<td>...</td>
</tr>
</tbody>
</table>

-ψ²/r₁A  -ψ²/r₁B  -ψ²/r₂A  -ψ²/r₂B  ψ²/r₁2  \( \frac{1}{2} \psi \nabla^2 \psi \)

Attraction  Repulsion  Kinetic Energy
Average of 10 runs (each contains 8000 sampling)

- Potential E
- Total E
- Kinetic E
- e-e repulsion

Spreadsheet
HF/STO-3G
Range and standard deviation of 10 runs

-4 -2 0 2

a. u.

\( \text{H}_2^+ \)   \( \text{H}_2 \)

Kinetic E   e-e repulsion

Potential E

Total E

Attraction

Range and standard deviation of 10 runs
Comparison of $\text{H}_2$ energy calculated using spreadsheet and using HF theory with various basis sets
Ex. 4. Exchange energy in H$_2^*$: first singlet vs. triplet excited states

No 2 electrons can have the same set of quantum numbers.

Electrons with same spin can better avoid each other than electrons with opposite spin, which reduces the e-e repulsion. This reduction of e-e repulsion is called exchange energy.

The e-e repulsion for the $S_1$ state and $T_1$ state:

$$\langle \frac{1}{r_{12}} \rangle = \frac{\int \psi \frac{1}{r_{12}} \psi d\tau}{\int \psi \psi d\tau} \approx \frac{\sum \psi^2 / r_{12}}{\sum \psi^2}$$

$$\psi_{S_1} = (\sigma_1 \sigma^* _2 + \sigma_2 \sigma^* _1) \quad \psi_{T_1} = (\sigma_1 \sigma^* _2 - \sigma_2 \sigma^* _1)$$
Ex. 5. Correlation energy in $\text{H}_2$: $\psi_{gs} + C_{ex} \psi_{ex}$

- 2-determinant wave function that includes a parametric constant $C_{ex}$ for the excited state determinant.
- Variational method to minimize $E_{corr}$.
- Minimum energy using the 2-determinant wave function compared to the HF energy with $C_{ex} = 0$. 

![Energy Diagram](image)
Ex. 5. Correlation energy in H\textsubscript{2}: $\psi_{gs} + C_{ex} \psi_{ex}$

Using Hartree product functions to calculate correlation energy approximately for a H\textsubscript{2} molecule:

$\psi_{gs} = \sigma_1 \sigma_2$ \hspace{1cm} w/o correlation

$\psi_{corr} = \sigma_1 \sigma_2 + C_{ex} \sigma_1^* \sigma_2^*$ \hspace{1cm} w/ correlation

$$E_{corr} \approx \frac{\sum (\psi_{corr}^2/r_{12})}{\sum \psi_{corr}^2} - \frac{\sum (\psi_{gs}^2/r_{12})}{\sum \psi_{gs}^2}$$
Acknowledgements

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• CWU Department of Chemistry
Questions?
Difference between $S_1$ and $T_1$ excited states:

$\sigma\alpha^1\sigma^*\beta^1$ (S1)  \hspace{1cm} \sigma^*\alpha^1\sigma^*\beta^1$ (T1)

w/o exchange  \hspace{1cm} w/ exchange

Use Hartree product $\psi_{HP} = \sigma_1\sigma^*_2$  \hspace{1cm} Use determinantal $\psi_{det}$
Exchange energy is the essentially the difference between repulsion of electrons with same spin vs. repulsion of electrons with opposite spin.

\[
\sigma_1 \sigma^*_2 - \sigma_2 \sigma^*_1 \]

\[
\text{Exchange } E \cong \frac{\sum \psi_{\text{det}}^2/r_{12}}{\sum \psi_{\text{det}}^2} - \frac{\sum \psi_{HP}^2/r_{12}}{\sum \psi_{HP}^2}
\]
\[- \frac{1}{2r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \left( \frac{\partial^2}{\partial \phi^2} \right) \right] \psi - \frac{1}{r} \psi = E \psi \]

\[- \frac{1}{2r^2} \left[ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right] e^{-r} \]

\[= \frac{1}{2r^2} \left[ \frac{\partial}{\partial r} \left( r^2 e^{-r} \right) \right] \]

\[= \frac{1}{2r^2} \left( 2re^{-r} - r^2 e^{-r} \right) \]

\[= \left( \frac{1}{r} - \frac{1}{2} \right) e^{-r} \]
H atom calculations

- Familiarize students with spreadsheet format.
- Calculation of kinetic energy and potential energy.
- Comparison to analytical solution.
Compilation

- Results from each student compiled using Google spreadsheet
- Results averaged and compared to HF/STO-3G calculations and experimental data.