PHYS4070 Project 1: Many Electron Atom

Semester 1 2023, 27 March

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Quantum theory is generally considered to be one of the most precise fields of physics, with models agreeing with experiment to within extreme margins of precision. In this project, we use quantum models of increasing complexity to numerically model the electron orbits of a lithium atom, validating our models against experimental measurements of the valence energy levels and the decay rate of the element’s first excited state.

# Part A: Background & Theory

The state of a many-body quantum system, e.g. the system of electrons bound to an atom, is described by a probabilistic wave function over all possible positions of all particles:

In simple models, we can describe the system as being a separable product of the wave functions of each individual particle:

Where each single particle wave function is an eigenstate of the ‘Single Particle Hamiltonian’, and the corresponding eigenvalues are the atom’s allowable electron energy levels:

The gradient term describes the electron’s kinetic energy, while the potential operator describes the combined effects of external electrostatic forces (in our case the attractive force of the atomic nucleus) and the interaction between the electrons.

In this project we are modelling atomic shells, and so it makes sense to adopt a spherical coordinate system. If we assume that each single-particle wave-function can be separated into a radial term and an angular term, we find that the solutions must be of the form:

Where are the ortho-normal set of spherical harmonics. Each possible solution / state is defined by the three integer quantum numbers :

* is akin to the wavenumber in the radial direction
* represents the angular momentum and angular wavenumber
* represents the spin of the electron, which can be up or down

Every one of these solutions states is orthogonal to all states.

As electrons are fermions, no two of them can share the same state, but states that differ only in ‘’ have the same energy. Each energy level ’’. can then hold up to two electrons, thanks to the two-fold degeneracy from ‘’. A historical naming convention for these states is to denote states with as an ‘s’ orbital, as a ‘p orbital’, e.g. we can say “there are up to two electrons in the 1s orbital”.

For an atom in its ground state, electrons will fill from its lowest energies upwards. For example, lithium atoms with electrons hold two tightly bound electrons in their core orbital and a single much more weakly bound valence electron in their orbital:

|  |  |  |
| --- | --- | --- |
|  | **,**  **s orbital** | **,**  **p orbital** |
|  |  |  |
|  |  |  |

If excited, the valence electron can transition up to the orbital. It remains here until decaying back to a lower state in some random time. The rate of decay (the probability of transitioning per unit time) for a transition from orbital ‘a’ to orbital ‘b’ is:

This decay rate increases as the energy gap between the orbitals increases, and as the amount of spatial overlap between the orbital’s wave functions increases:

For the decay from 2p to 2s, , and the timescale of decay has been experimentally measured as:

Note that scales with the cube of energies, and that is highly sensitive to the amount of overlap in the waves. If the waves peaks are narrow, even small changes in our solution can have a large effect on the decay rate, and so even small changes to our model can impact our estimate of significantly.

**Solving the Radial Hamiltonian**

Instead of the radial component , it ends up begin convenient to define our working in terms of:

With this change, the single particle Hamiltonian simplifies to a much friendlier “radial Hamiltonian” , which still encodes our energy levels as eigenvalues. Using ‘atomic units’ where all natural constants are unity, this looks like:

It is also much easier to calculate expectation values for any radial function in this form:

Because the spherical harmonics are orthonormal, the angular part of this integral vanishes, and the form of removes the remaining spherical geometry:

For our purposes, are real functions, so this becomes:

For example, the average position of an orbital is simply:

# Part B1 – Hydrogen-Like Lithium

### Modelling

The simplest model of the lithium atom is one in which we completely ignore electron-electron interaction. Ignoring the fact that the atom’s nucleus is itself a quantum object, we can treat it as a positive point charge of charge ‘Z’ with a simple electrostatic potential, so that the radial Hamiltonian looks like:

Where represents the electron-electron interactions. In this form, we can see that ‘’ works like angular momentum or kinetic energy, producing a ‘centrifugal force’ that makes the electrons binding potential less negative. For simplicity, add this to the ‘effective potential’:

To solve the eigenstates of this Hamiltonian, we can assume that any given solution is a linear combination of some set of basis functions :

Such that the Hamiltonian equation for eigenstate becomes:

If we pre-multiply by another basis function, we get a linear set of equations:

Which we can describe as a matrix eigenvalue problem with the coefficients forming the eigenvector:

Where the matrices are defined:

For this system to be solved, we need an equal number of basis states to the number of waves we are trying to solve to get square matrices. We need a at least few dozen basis functions to make a basis function robust enough to describe arbitrary wave shapes, and so we end up solving more wave states than are physically meaningful.

The B matrix elements only require integration of our basis functions:

While the Hamiltonian terms require a bit of manipulation:

This first term can be described in terms of first derivatives, which are numerically more convenient:

After solving for , we reassemble our wavefunctions from the basis by .

### Program

Our definitions of the H and B matrices include inner products that are integrals over a semi-infinite domain, . We run into singularities at , and numerically integrating an infinite range requires complicated reparameterization, so we instead limit our integrals to some minimum and maximum value:

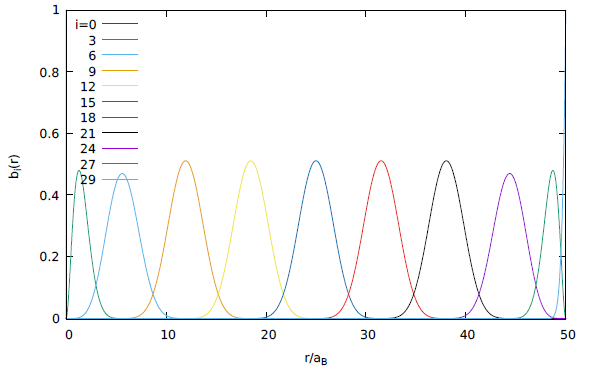
We know to avoid the infinite potentials at the nucleus, and we also know that as the electrons cannot exist too far from the atom. Provided and are large enough to encapsulate the wavefunctions of interest, our ‘cut-off’ of the domain will have only a minor effect on our results.

We evaluate functions over an evenly spaced radial grid of points:

And approximate integrals using a Simpsons’ rule summation:

This integration is performed by the vint() function defined in vector\_utils.cpp.

In this project, we use the “b-splines” as our basis states. B-splines are k-order piecewise polynomials, with a set of splines defined over a fixed domain and each spline forming a bell-curve like knot over a sub-domain. If we exclude the first two b-splines and the last b-spline in the set, our basis functions will already obey our boundary conditions for , and so we don’t need to worry about enforcing these in our solutions.

  
**A Subset of 31 k=7 B-Splines Over**

Constructing the Hamiltonian matrix requires evaluating the derivatives of these splines, for which we use central finite differences:

For consistency, we use the same interval as the r-grid,

Eigenstates are solved using the Fortran library LAPACK, specifically the DYSGV routine. This routine is accessed in a more user-friendly format in the LPsolvers.cpp file. Because the b-splines are not normalized, neither are our solutions when using:

Instead, we re-normalize after the fact with:

This routine is contained in the solve\_energies() function, which takes the b-splines and their derivatives as external inputs, as these can be re-used between different physical setups.

### Results

The following results, and all sections after unless specified, use parameters:

For a bare nucleus, we have approximate expressions for the energy levels and mean radius:

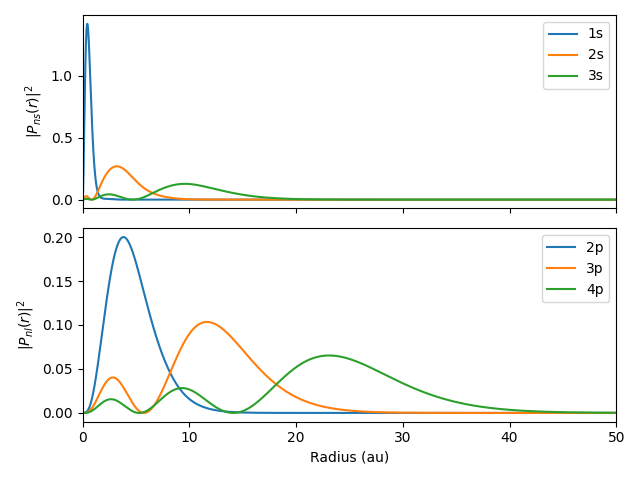
Using our solver for l and p orbitals, we find that is gives close fits to these analytical expressions. The largest deviations are at , specifically the closely bound 1s orbital. This is a result of numerical error arising form and the rapid changes in the potentials that occur at . As we move to more complicated models in later sections, the waves will move away from the nucleus and mitigate these issues. We also see that for all n. This is due to the ‘centrifugal’ term in our potential being strictly positive.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  | | --- | --- | --- | --- | | n |  | | | |  | **,**  **s orbital** | **,**  **p orbital** | | 1 | -4.500 | -4.398 |  | | 2 | -1.125 | -1.134 | -1.122 | | 3 | -0.500 | -0.505 | -0.500 | | 4 | -0.281 | -0.283 | -0.281 | | 5 | -0.180 | -0.181 | -0.180 | | 6 | -0.125 | -0.126 | -0.125 | | 7 | -0.092 | -0.092 | -0.092 | | 8 | -0.070 | -0.071 | -0.070 | | 9 | -0.056 | -0.056 | -0.056 | | 10 | -0.045 | -0.045 | -0.045 |   **vs n for Hydrogen-Like Atom, Model vs Sim Comparison** | |  |  |  |  |  | | --- | --- | --- | --- | --- | | n |  | | | | | **,**  **s orbital** | | **,**  **p orbital** | | | **Model** | **Sim** | **Model** | **Sim** | | 1 | 0.50 | 0.55 |  | | | 2 | 2.00 | 1.97 | 1.00 | 1.67 | | 3 | 4.50 | 4.45 | 3.50 | 4.17 | | 4 | 8.00 | 7.93 | 7.00 | 7.67 | | 5 | 12.50 | 12.42 | 11.50 | 12.17 | | 6 | 18.00 | 17.90 | 17.00 | 17.67 | | 7 | 24.50 | 24.38 | 23.50 | 24.17 | | 8 | 32.00 | 31.87 | 31.00 | 31.67 | | 9 | 40.50 | 40.35 | 39.50 | 40.17 | | 10 | 50.00 | 49.83 | 49.00 | 49.67 |   **vs n for Hydrogen-Like Atom, Model vs Sim Comparison** |

The estimate for similarly becomes more accurate at large r, but performs worse for the p orbitals at low r.

Plotting the first few wave functions for both ‘s’ and ‘p’, we can see the familiar pattern of higher ‘n’ giving more ‘wobbles’ in the wave functions. However, the number depends not on ‘n’, but the position of the wave in the energy sequence for that orbital, e.g. the 2p orbital is has only a single ‘bump’ despite being a orbital.

As we go to higher energies at higher ‘n’ and ‘l’, the wave functions move away from the negative potential well of the nucleus, and become broader as they are less constrained.

  
**First 3 Wave Densities for Hydrogen-Like Atom**

Using these energies and wavefunctions, we find that the decay timescale is huge. For a hydrogen-like atom, l has no effect on the energies and the lack of e-e repulsion constrains the wave functions to low radius:

Resulting in an unreasonably long decay timescale:

Even this is value is an artefact of numerical imprecision. In the ideal limit of , we would get for and .

**Effect of**

We can see a shortfall of our choice of basis function if we lower to an unreasonably low value, say . Our b-splines now only span up to a set limit, which is the same as restricting the electrons to . This causes the waves to ‘bunch up’ inside, fitting the same general shape into a small domain.

|  |  |
| --- | --- |
| **First 3 waves, Hydrogen-Like Atom, Short Domain** | **First 10 waves, Hydrogen-Like Atom, Short Domain** |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| This doesn’t just distort the shape of the wavefunction, it also impacts our recovered energies. Because the waves have the same number of ‘wobbles’ over a shorter domain, their derivatives become proportionally higher, increasing their kinetic energy in the Hamiltonian’s term. This is worse for higher order modes, and can even result in them having positive energies. This is non-physical, as a positive energy would mean an electron in that state isn’t bound. | |  |  |  | | --- | --- | --- | | n |  | | | **,**  **s orbital** | **,**  **p orbital** | | 1 | -4.530 |  | | 2 | -1.129 | -1.125 | | 3 | -0.501 | -0.500 | | 4 | -0.282 | -0.281 | | 5 | -0.177 | -0.177 | | 6 | -0.086 | -0.089 | | 7 | 0.036 | 0.028 | | 8 | 0.189 | 0.175 | | 9 | 0.372 | 0.352 | | 10 | 0.583 | 0.556 |   **vs n for Hydrogen-Like Atom, Short Domain** |

# Part B2 – Neutral Lithium (Green’s Approximation)

### Modelling

Our simple hydrogen-like model gives reasonable looking results, but completely ignores the electrostatic effects of the electrons themselves. This is obviously non-physical, as it treats the entire atom as being negatively charged. A simple way to model the electron charge is to use Greens Function:

|  |  |
| --- | --- |
| Where, for us, and . The effect of green’s function is to gradually transition from a positive nucleus at small r, to a near-neutral one at large r:  The remaining positive charge at is due to the electrons not being repelled by themselves, they can only see electrons ‘below’ them. This is a crude approximation, but makes a significant difference to our results. | **Greens Function Acting on Potential** |

**First Order Perturbation**

Modelling e-e interaction with green’s function isn’t much more than a guess at the ‘sort of shape’ we expect to see, but still acts as a good first approximation. In lithium, we can do one better in that we know the two bound electrons in the core have a spherically symmetric distribution, and are the only source of e-e interaction that affects the valence electron.

For each radius that the 1s electrons might be at, , it creates a repulsive potential at all greater radii , and has no effect at :

But, when , the core electrons are affected by the valence electron in a similar way:

With a factor of 2 for the two electrons in the core, this gives an overall potential:

This is called the ‘direct potential’. Because it depends on the core electron wave function , we cannot evaluate it explicitly. Instead, we can estimate the effect assuming , getting a first order perturbation to the energies with:

Where we solve and using Green’s function and get a better estimate of the energies .

### Results

|  |  |
| --- | --- |
| **Wave Density for Bare Nucleus (Top) & Using Green’s Function (Bottom)** | Including Green’s function in our potential, we immediately notice that the wave functions spread out to much larger radii, most strongly effecting the valence states. This is to be expected: the core orbitals are at low radii where while the 2s and 2p states, positioned further out, see the effects of the electron screening. Specific to our goal of finding , we find:  Almost four times what we had in the hydrogen-like atom. |

We also find that the energies become less negative: with the electrons counteracting the nucleus’s attraction, the orbitals are less tightly bound. Green’s function over-estimates the screening, however, and applying the linear perturbation shifts the energies to be slightly more negative.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  |  |  | | --- | --- | --- | --- | --- | | n |  | | | | | **Greens Function Only** | | **With Perturbation** | | | **S  Orbital** | **P  Orbital** | **S  Orbital** | **P Orbital** | | 1 | -0.846 |  | -1.602 |  | | 2 | -0.157 | -0.125 | -0.204 | -0.130 |   **Important Energies/w Simple E-E Interaction** | **Potential Functions For Greens Function & First Order Hartree Correction** |

While we’ve broken the energy degeneracy, the sensitivity of the decay time to the energy levels means that our estimates are still quite far off, though with the perturbation we are at least closing in to a reasonable value:

|  |  |  |  |
| --- | --- | --- | --- |
|  | Greens Func Only | With Perturbation | Using |
| *(au)* | 0.0314 | 0.0742 | 0.0680 |
| *(ns)* | 181.3 | 13.9 | 18.1 |

**Decay Rate Comparison for Greens Function & First Order Hartree Correction**

# Part B3 – Self-Consistent Hartree Procedure

### Modelling

In Part B2.1, we found that the e-e potential from the core electrons required foreknowledge of the 1s wavefunction:

Though we can’t solve for and simultaneously, we can iterate our solution until our potential and wave 1s wave function converge on a self-consistent solution. For each iteration, we find the new e-e potential, use it to populate our Hamiltonian matrix, and use this to solve our new wave function:

Where we use as the starting point for our iteration as per part B2.

### Program

We follow a similar process to parts B1 and B2, but iterating on the s-orbital wave functions until convergence is achieved. Two functions have been written to perform the operation:

* Hartree(), which re-uses the solve\_energies() function from parts B1 and B2
* Hartree\_fast(), which uses the solutions of the previous iteration as the basis for the next iteration. This has two advantages:
  + This basis is already orthonormal, so ‘B’ is an identity matrix and we can use LAPACK’s DSYEV routine to solve
  + As the system converges, H becomes near-diagonal, and requires less computational power to calculate the eigenstates and eigenvalues

Hartree\_fast()requires the derivatives of the basis states to populate the H matrix each iteration. This is accomplished with the vdiff() function, which uses central finite differences over the vectors, except for the start and end points which use forward and backward differences respectively:

In both cases, convergence is measured by the fractional change in the s-orbital energies from one iteration to the next. Both and Hartree()and Hartree\_fast()take the tolerance (default 1E-6), maximum number of iterations (default 40) and number of s-orbital energies to check for convergence (default 5). Results here are for the standard method.

The ‘l’ orbital solutions depend only on the 1s wave, and so are calculated after iterations of the s orbitals have concluded.

### Results

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  | | --- | --- | --- | | Iteration number |  |  | | 1 | -1.849 | 5.6E-01 | | 2 | -1.253 | 4.8E-01 | | 3 | -1.443 | 1.3E-01 | | 4 | -1.362 | 6.0E-02 | | 5 | -1.393 | 2.3E-02 | | 6 | -1.380 | 9.1E-03 | | 7 | -1.385 | 3.6E-03 | | 8 | -1.383 | 1.4E-03 | | 9 | -1.384 | 5.7E-04 | | 10 | -1.384 | 2.2E-04 | | 11 | -1.384 | 8.9E-05 | | 12 | -1.384 | 3.5E-05 | | 13 | -1.384 | 1.4E-05 | | 14 | -1.384 | 5.6E-06 | | 15 | -1.384 | 2.2E-06 | | 16 | -1.384 | 8.8E-07 |   **Hartree-Procedure Values For** | Iterating the Hartree correction, we find that the 1s core energy exponentially converges towards a slightly better value final value, though still a bit high. Convergence is exponential, with fluctuations decreasing by ~60% per step, meaning we need ~5 iterations for another order of magnitude of precision.    **Hartree-Procedure Convergence For** | |
| Using these solutions, we get , not a large change from the value from using Green’s function in B2. We can confirm this visually by comparing the wave functions for these results and seeing that they have changed only slightly (right). Overall, the wave-functions have shifted slightly inwards, and have lower spreads. | | **Wave Density For Pure Greens Function (Clear) & Full Hartree (Solid)** | |

Our decay rate estimate has gotten worse, with the valence energies drifting further from experiment, in both cases slightly less negative than they should be.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Greens Func Only | With Perturbation | Full Hartree | Experimental Values |
|  | -0.157 | -0.204 | -0.183 | -0.198 |
|  | -0.125 | -0.130 | -0.127 | -0.130 |
| *(au)* | 0.0314 | 0.0742 | 0.0556 | 0.0680 |
| *(ns)* | 181.3 | 13.9 | 43.13 | 27.10 |

**Decay Rate Comparison for Full Hartree Procedure**

# Part B4 –Hartree-Fock

### Modelling

In the introduction, we assumed that the overall system state could be separated cleanly into a product of state-kets for each electron:

As electrons are fermions, this actually isn’t true. must be anti-symmetric, i.e.:

E.g., a two-electron system must look like:

This change has implications for our energies. For brevity, write the state as:

If there is any interaction between the electrons, this gives rise to an ‘exchange energy’. Continuing the 2-particle examples, suppose we have an interaction term in the Hamiltonian. The expectation value of this on an antisymmetric ket is:

The second of these terms appears only by virtue of the system’s antisymmetry. This manifests as an extra term in our Hamiltonian matrix:

Here, is a more a more general form of the electrostatic shells we used to get the direct potential in part B2:

And is a normalizing coefficient that appears due to the angular component of our wave functions. Because we are concerned only with ‘s’ and ‘p’ orbitals, there are only two coefficients of interest:

Much like the Hartree procedure, the Hamiltonian now includes terms that depend on the wave functions, and so must be solved iteratively.

### Program

To apply the Hartree-Fock procedure, we use the same methods as the pure Hartree procedure: checking the convergence of the energy levels to within a tolerance. The only major difference is that we must have two iteration loops: one for the s orbitals and one for the p orbitals. The l orbitals depend on the s orbitals, and so we iterate to solve the s orbitals first.

Instead of starting from Green’s function, the pure Hartree procedure is applied to a tolerance 10x greater than specified, and this solution is used as an input to the Hartree-Fock function.

As with the Hartree procedure, two functions have been written:

* Hartree\_fock(), which populates the H matrix using B splines as a basis
* Hartree\_fock\_fast(), which uses the orthonormal basis of the previous iterations solutions.

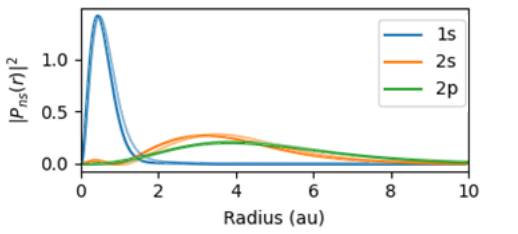
As with part B3, results here are for the standard method.

### Results

Using our Hartree results as a starting point, the Hartree-Fock procedure converges much closer to experiment. It also converges much faster, with the fractional energy change in 1s dropping by ~87% each iteration, almost an entire order of magnitude per step.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| |  |  |  | | --- | --- | --- | | Iteration number |  |  | | 1 | -2.813 | 5.08E-01 | | 2 | -2.737 | 2.77E-02 | | 3 | -2.728 | 3.19E-03 | | 4 | -2.727 | 4.23E-04 | | 5 | -2.727 | 5.80E-05 | | 6 | -2.727 | 8.09E-06 | | 7 | -2.727 | 1.14E-06 | | 8 | -2.727 | 1.61E-07 |   **Hartree-Procedure Values For** | **Hartree-Fock Convergence For** |

Modelling the exchange energy does not have a dramatic effect on the shape of our solution waves: they shift slightly inwards and become less broad compared to the pure Hartree case. We can put a number to this small change by noting that , only a marginal change from the pure Hartree case.

  
**Wave Density For Pure Hartree (Clear) & Hartree-Fock (Solid)**

Where we do see significant changes is in the valence energies. The exchange markedly decreases the 2s orbital energy, increasing the energy gap to 2p and bringing our estimate of the decay time remarkably close to the experimental value.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Hartree | Hartree-Fock | Experimental Values |
|  | -0.183 | -0.1963 | -0.198 |
|  | -0.127 | -0.129 | -0.130 |
| *(au)* | 0.0556 | 0.0673 | 0.0680 |
| *(ns)* | 43.13 | 27.10 | 27.10 |

**Decay Rate Comparison for Hartree & Hartree Fock**

We can understand the effect of the Hartree-Fock procedure in that the exchange energy represents the effects of electrons as fermions. In a broad view, fermions don’t “like” to be similar to one another, and introducing the signature antisymmetry of the fermion causes waves of similar quantum numbers to space their energies out more broadly. For example, looking at the relative energy gap between states with the same n, we see that they have all become proportionally larger compared to the pure Hartree case:

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| n | Hartree | | | Hartree-Fock | | |
|  |  |  |  |  |  |
| 1 | -1.384 |  |  | -2.727 |  |  |
| 2 | -0.183 | -0.127 | 36% | -0.196 | -0.129 | 41% |
| 3 | -0.071 | -0.056 | 23% | -0.074 | -0.057 | 26% |
| 4 | -0.037 | -0.032 | 17% | -0.038 | -0.032 | 19% |
| 5 | -0.023 | -0.020 | 13% | -0.024 | -0.020 | 15% |

**Energy Difference Comparisons for Hartee & Hartree-Fock Solutions**

We see a similar pattern when looking at energies with the same ‘l’ but different ‘n’: the gaps are all larger. It’s this energy separation that increases towards the experimental value, and corrects out estimate of the decay rate.

# Conclusion

Through the example of a lithium atom, we can see both the extreme precision of quantum theory and the complexity required in our modelling to get accurate results. While simple models can approximate energy levels, they fail to recover more sensitive properties like the decay rate of excited states for even small simplifications. Future work should look at including orbitals of higher ‘l’ values so that atoms with can be modelled, and should seek to reduce numerical error by either extending the integration range / increasing grid spacing, or using reparameterization to properly model the full range of radii.

# Appendix A: Alternate Iterator Methods

For parts B3 and B4, two iterators are coded in potentials\_and\_solvers.cpp for each problem. In the ‘standard’ iterators, the b-splines are used as the basis functions for every iteration, while the ‘alternate’ iterators uses the orthonormal solutions to the previous iteration. For the same grid parameters as used in the rest of this report, the alternate iterators give similar but slightly worse results:

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Normal Iterator | | Alternate Iterator | | Experimental Values |
|  | Hartree | Hartree-Fock | Hartree | Hartree-Fock |
|  | -0.183 | -0.1963 | -0.1827 | -0.1959 | -0.198 |
|  | -0.127 | -0.129 | -0.1275 | -0.1291 | -0.130 |
| *(au)* | 0.0556 | 0.0673 | 0.0552 | 0.0668 | 0.0680 |
| *(ns)* | 43.13 | 27.10 | 43.88 | 27.54 | 27.10 |

This imprecision is likely from the worse estimate of , with the alternate iterator using a in its finite differences and defaulting to the less precise forward finite difference near .

The convergence properties are unaffected, with both Hartee and Hartee-Fock converging at the same exponential rate for their alternate versions.

