

Semirelativistic Kinetic Energy with Correlated Gaussian Method

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Bachelor's project

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June 2022

Abstract

In this thesis the simple quantum system of the hydrogen atom has been defined and investigated by stochastic variation. The ground states of several Hamiltonians have been estimated while working in a basis consisting of gaussian functions. In this basis matrix elements for different constituents of the Hamiltonians have been derived specifically the relativistic kinetic energy in momentum space. The simulated ground state values have been compared to values obtained through perturbation and statistical considerations have been made. Ultimately the stochastic variation method with correlated gaussians have been found to be comparable to a perturbation calculation.

Resume på dansk

I dette projekt er det simple kvantesystem i form af hydrogen atomet, blevet defineret og undersøgt ved stokastisk variation. Grundtilstanden af forskellige Hamiltoner er blevet estimeret i en basis bestående af gaussiske funktioner. I denne basis er matrixelementerne for disse Hamiltoner blevet udledt specielt for den relativistiske kinetiske energi i impulsrum. De simulerede grundtilstandsværdier er blevet sammenlignet med værdier opnået gennem en perturbationsberegning og statistiske overvejelser er blevet gennemgået. Den stokastiske variationsmetode med korrelerede gausser har vist sig at være sammenlignelig med en perturbationsberegning.

Colophon

Semirelativistic Kinetic Energy with Correlated Gaussian Method

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Layout and typography based on template from Jakob Lysgaard Rørsted
Typeset by the author using L^AT_EX and the memoir document class, using
Linux Libertine and Linux Biolinum 12.0/15.36996pt.

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CHAPTER 1

Introduction

Modeling quantum mechanical systems is one of the primary endeavors in theoretical physics. The more difficult a subject is to study physically, the more weight lies in theoretical investigation. The mathematical formulation of quantum theory is quite well established making for a great foundation when investigating the physical outcomes of ideas and propositions.

One of the most important, yet potentially undervalued aspects of theoretical physics, is the development of the tools that are essential for working within the established theoretical framework. Once within a paradigm the real scientific work is making sure the theory is as sound as possible as well as developing the tools that allow for the theory to be utilized.

The hydrogen atom is a great simple system to act as playground for the development of tools. This is because of the inherent simplicity of a two body system as well as the vast amount of well known properties which are useful for comparison.

Working with special relativity together with the Schrödinger equation might be questionable, as the properties studied might be better encapsulated by more sophisticated theories. It is however always of interest to have good approximations that are easier to work with but more importantly, the methods used in this thesis is expected to be useful in other circumstances.

Theoretical background

2.1 Quantum system

The methods outlined in this thesis is particularly motivated by the desire to study nuclear interactions by way of explicitly calculating meson exchange as quantum bodies using the standard Schrödinger equation governing the motion of quantum particles as described in [2]. For instance the deuterium nucleus would be modeled with the state of the nucleus itself as well as a state with an additional particle, for instance the σ meson. The state might look like this

$$\psi = \begin{pmatrix} \psi_{n,p}(\mathbf{r}_n, \mathbf{r}_p) \\ \psi_{n,p,\sigma}(\mathbf{r}_n, \mathbf{r}_p, \mathbf{r}_\sigma) \end{pmatrix} \quad (2.1)$$

where the system is in a superposition of having the meson present or not. The Hamiltonian might look like this

$$H = \begin{pmatrix} K_n + K_p & W \\ W & K_n + K_p + K_\sigma + m_\sigma \end{pmatrix} \quad (2.2)$$

with the energies of the particles as well as the W operators responsible for the coupling of the two subsystems. Additionally energy required for creating the particle is included as the mass.

In this thesis a slightly simpler example will be examined where only one system is present and thus no coupling is necessary specifically the proton-electron system of the hydrogen atom. Multiple Hamiltonians will be examined, involving the regular coulomb potential as well as both classical kinetic energy and a relativistic kinetic energy, making the model semi relativistic.

$$H = K_{classic} + V_{Coulomb} \quad (2.3)$$

$$H = K_{classic} + K_{relativistic} + V_{Coulomb} \quad (2.4)$$

Additionally for model control the following hamiltonian will be used

$$H = K_{classic} + V_{SHM} \quad (2.5)$$

where V_{SHM} is the simple harmonic oscillator potential. The Hamiltonians here are one dimensional as the two body system can be reduced by using the center of mass frame. This can be applied generally as explained in the following section.

2.2 Coordinate transformation

When dealing with an N -body system it can be useful to work in center of mass frame using a different set of coordinates. One such set of coordinates is the Jacobi coordinates which re-expresses the system in terms of the center of mass and the relative position of the particles with respect to each other. Since the relative coordinates and the center of mass coordinate are completely independent one can make the energy associated with the center of mass equal to zero and thus reduce the N -body problem to an $N - 1$ -body problem.

2.3 Solving energy states

When analyzing quantum mechanical systems the most meaningful value is often the energy which is typically found as the eigenvalues of the Schrödinger equation.

$$\hat{H} |\psi\rangle = E |\psi\rangle \quad (2.6)$$

Here the wave function is given in some basis $\{|e_i\rangle, i = 1, \dots, n\}$ with a vector \mathbf{c} being the representation of the state in the basis.

$$|\psi\rangle = \sum_{i=1}^n c_i |e_i\rangle \quad (2.7)$$

Noting here that n is the number of elements in the basis not the number of particles N . Now taking the inner product of the whole expanded Schrödinger equation from the left with some basis function $|e_k\rangle$, yields the following

$$\sum_{i=1}^n \langle e_k | \hat{H} | e_i \rangle c_i = E \sum_{i=1}^n \langle e_k | e_i \rangle c_i \quad (2.8)$$

which can be written in matrix form as

$$\mathcal{H}\mathbf{c} = E\mathcal{N}\mathbf{c} . \quad (2.9)$$

This is the generalized eigenvalue where \mathcal{H} is again the Hamiltonian matrix and \mathcal{N} is the overlap matrix. This can be solved using a decomposition method when the overlap matrix is positive definite, and in thesis an implementation of this will be used using the `scipy.linalg.eigh` function in Python.

2.4 Stochastic variation

The fundamental property of quantum systems that fuels the method to be used is the variational principle. The principle ensures that for an arbitrary normalized function, the expectation value of the Hamiltonian will stay above the the actual ground state energy, expressed like this:

$$E_1 \leq \langle \psi | \hat{H} | \psi \rangle \quad (2.10)$$

This principle allows for estimating the ground state energy of the system by finding states with as low energy as possible. A method for this optimization would be complete stochastic optimization in which pseudo random states are generated in large amounts in an attempt to find the lowest energy for a good estimate. The effectiveness of this approach depends on the amount of parameters and how well the basis suits the Hamiltonian.

Alternatively stochastic variation could involve saving individual basis elements at a time and then expanding using optimized basis elements. This can be more efficient in systems with more parameters. Additionally some deterministic optimization could also be involved.

2.5 Vector integral identity

The following vector integral will be used throughout the thesis and as such shall be derived.

$$I = \int d^3\vec{x}_1 d^3\vec{x}_2 \dots d^3\vec{x}_N e^{-\mathbf{x}^T B \mathbf{x} + \mathbf{v}^T \mathbf{x}} = \left(\frac{\pi^N}{\det(B)} \right)^{\frac{3}{2}} e^{\frac{1}{4} \mathbf{v}^T B^{-1} \mathbf{v}} \quad (2.11)$$

Where B is a real positive definite symmetric matrix and as such can be diagonalized using an orthogonal transformation. The orthogonal transformation matrix O is introduced such that $B = O D O^T$ where D is diagonal. Naturally the associated coordinate transformation is given as $y = O x$. Using these tools the integral can be calculated. Due to cumbersome notation the arrows over the 3D-vectors will be left out.

$$\begin{aligned} I &= \int d^3 x_1 d^3 x_2 \dots d^3 x_N e^{-\mathbf{x}^T O O^T B O O^T \mathbf{x} + \mathbf{v}^T \mathbf{x}} \\ &= \int d^3 y_1 d^3 y_2 \dots d^3 y_N e^{\sum_{i=1}^N -D_{ii} y_i^2 + (\mathbf{v}^T O)_i y_i} \\ &= \prod_{i=1}^N \int d^3 y_i e^{-D_{ii} y_i^2 + (\mathbf{v}^T O)_i y_i} \end{aligned}$$

By completing the square it is possible to rearrange the exponent such that the integral reduces to the simple gaussian.

$$\begin{aligned} I &= \prod_{i=1}^N \int d^3 y_i e^{-D_{ii} \left(y_i - \frac{(\mathbf{v}^T O)_i}{2D_{ii}} \right)^2 + \frac{(\mathbf{v}^T O)_i^2}{4D_{ii}}} \\ &= \prod_{i=1}^N e^{\frac{(\mathbf{v}^T O)_i^2}{4D_{ii}}} \int d^3 y_i e^{-D_{ii} \left(y_i - \frac{(\mathbf{v}^T O)_i}{2D_{ii}} \right)^2} \end{aligned}$$

Since the integral is over all of space the constant shift in the exponent can be eliminated by a simple coordinate transformation $\omega_i = y_i - \frac{(\mathbf{v}^T O)_i}{2D_{ii}}$ after which the simple gaussian integral is trivial.

$$\begin{aligned} I &= \prod_{i=1}^N e^{\frac{(\mathbf{v}^T O)_i^2}{4D_{ii}}} \int d^3 \omega_i e^{-D_{ii} \omega_i^2} \\ &= \prod_{i=1}^N e^{\frac{(\mathbf{v}^T O)_i^2}{4D_{ii}}} \left(\frac{\pi}{D_{ii}} \right)^{\frac{3}{2}} \end{aligned}$$

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Now finally by using the properties of the diagonal and orthogonal matrices the product can be expanded into the vector forms again.

$$\begin{aligned} I &= \left(\frac{\pi^N}{\det(D)} \right)^{\frac{3}{2}} e^{\frac{1}{4} \mathbf{v}^T O D^{-1} O^T \mathbf{v}} \\ &= \left(\frac{\pi^N}{\det(B)} \right)^{\frac{3}{2}} e^{\frac{1}{4} \mathbf{v}^T B^{-1} \mathbf{v}} \end{aligned}$$

Correlated Gaussians

3.1 Gaussian functions

3.1.1 Definition

This thesis will work with quantum states expressed in a basis of gaussian functions. The motivation for this relates to the nature of gaussian function. Integrals involving gaussian are often analytical and converges when multiplied with many unbounded functions, which makes them especially nice to work with. The functions are defined using their projection onto a position vector.

$$\langle \mathbf{r} | \mathbf{g} \rangle = \exp \left(- \sum_{i,j=1}^N A_{i,j} \vec{r}_i \cdot \vec{r}_j + \sum_{i=1}^N \vec{s}_i \cdot \vec{r}_i \right) \quad (3.1)$$

Introducing the size N column vector \mathbf{r} with elements consisting of N three dimensional position vectors \vec{r}_i as well as the $N \times N$ correlation matrix A and the column vector \mathbf{s} with N shift vectors \vec{s}_i the function can be expressed more compactly,

$$\langle \mathbf{r} | \mathbf{g} \rangle \equiv e^{-\mathbf{r}^T A \mathbf{r} + \mathbf{s}^T \mathbf{r}} \equiv \mathbf{g}_{A,s}(\mathbf{r}) \quad (3.2)$$

using the following notation with the matrices and vectors:

$$\mathbf{r}^T A \mathbf{r} \equiv \sum_{i,j=1}^N A_{i,j} \vec{r}_i \cdot \vec{r}_j \quad \mathbf{s}^T \mathbf{r} \equiv \sum_{i=1}^N \vec{s}_i \cdot \vec{r}_i$$

Additionally an even simpler notation will be used for just the vector itself:

$$|A, \mathbf{s}\rangle \equiv |\mathbf{g}\rangle$$

It will be valuable to make the requirement that the A matrix must be positive definite. This can be accomplished by defining it using a size N column vector \mathbf{w} with the property that all components equal zero except two where $w_i = 1 = -w_j$. Generating a positive definite matrix can be done like this

$$A = \sum_{i < j} \mathbf{w}_{ij} \mathbf{w}_{ij}^T \alpha_{ij} \quad (3.3)$$

where \mathbf{w}_{ij} denotes, through abuse of notation, the \mathbf{w} vector whose i 'th and j 'th entries are 1 and -1. This ensures the required positive definiteness.

Applying a coordinate transformation as described earlier is easily done through this definition. By transforming the \mathbf{w} vectors using the transformation matrix and removing the row concerning the center of mass, the A matrix is now an $(N - 1) \times (N - 1)$ matrix retaining its positive definiteness as required.

In the case of the proton-electron system, this transformation leaves the A matrix as a scalar. Similarly, while matrix elements will be derived using the shift vector \mathbf{s} , only the ground state of systems will be examined in this thesis and as such the particles will be in a zero angular momentum state. This leaves the shift vector to be zero.

3.1.2 Momentum space

It will be useful later to calculate matrix elements in momentum space, thus the projection of \mathbf{g} onto \mathbf{k} is needed. It is known that the eigenfunction of the momentum operator in position space is exactly the fourier transform, meaning that projecting the state onto momentum space is simply taking the fourier transform of the position space vector. This is particularly practical in the case of gaussians, as the fourier transform of a gaussian function is itself a gaussian.

Using the relation of the fourier transform the momentum space vector

is found:

$$\begin{aligned}
\langle \mathbf{k}|A, \mathbf{s}\rangle &= \tilde{\mathbf{g}}_{A, \mathbf{s}}(\mathbf{k}) = \int d^{3N} \mathbf{r} \mathbf{g}_{A, \mathbf{s}}(\mathbf{r}) e^{-i\mathbf{k} \cdot \mathbf{r}} \\
&= \int d^{3N} \mathbf{r} e^{-\mathbf{r}^T A \mathbf{r} + \mathbf{s}^T \mathbf{r} - i\mathbf{k}^T \mathbf{r}} \\
&= \int d^{3N} \mathbf{r} e^{-\mathbf{r}^T A \mathbf{r} + (\mathbf{s}^T - i\mathbf{k}^T) \mathbf{r}}
\end{aligned}$$

Here $\tilde{\mathbf{g}}$ refers to the fourier transform $\mathcal{F}[\mathbf{g}]$ of \mathbf{g} . The $N \times 3$ -dimensional integral is denoted using the differential $d^{3N} \mathbf{r}$ using the column vector \mathbf{r} meaning $d^3 \vec{r}_1 d^3 \vec{r}_2 \dots d^3 \vec{r}_N$. Now applying the vector integral identity (2.11) and subsequently using linearity of real scalar products one obtains:

$$\begin{aligned}
&= \left(\frac{\pi^N}{\det(A)} \right)^{\frac{3}{2}} e^{\frac{1}{4}(\mathbf{s}^T - i\mathbf{k}^T) A^{-1} (\mathbf{s} - i\mathbf{k})} \\
&= \left(\frac{\pi^N}{\det(A)} \right)^{\frac{3}{2}} e^{\frac{1}{4} \mathbf{s}^T A^{-1} \mathbf{s} - \frac{1}{4} \mathbf{k}^T A^{-1} \mathbf{k} - \frac{i}{4} \mathbf{s}^T A^{-1} \mathbf{k} - \frac{i}{4} \mathbf{k}^T A^{-1} \mathbf{s}} \\
&= \left(\frac{\pi^N}{\det(A)} \right)^{\frac{3}{2}} e^{\frac{1}{4} \mathbf{s}^T A^{-1} \mathbf{s} - \frac{1}{4} \mathbf{k}^T A^{-1} \mathbf{k} - \frac{i}{2} \mathbf{s}^T A^{-1} \mathbf{k}} \\
&= \left(\frac{\pi^N}{\det(A)} \right)^{\frac{3}{2}} e^{\frac{1}{4} \mathbf{s}^T A^{-1} \mathbf{s}} \mathbf{g}_{\frac{1}{4} A^{-1}, -\frac{i}{2} A^{-1} \mathbf{s}}(\mathbf{k})
\end{aligned}$$

Again for brevity and practicality later, the following function is introduced:

$$\mathcal{M}(A, \mathbf{s}) \equiv \left(\frac{\pi^N}{\det(A)} \right)^{\frac{3}{2}} e^{\frac{1}{4} \mathbf{s}^T A^{-1} \mathbf{s}} \quad (3.4)$$

which allows the momentum space vector be written compactly as

$$\langle \mathbf{k}|A, \mathbf{s}\rangle = \mathcal{M}(A, \mathbf{s}) \mathbf{g}_{\frac{1}{4} A^{-1}, -\frac{i}{2} A^{-1} \mathbf{s}}(\mathbf{k}). \quad (3.5)$$

3.2 Matrix elements

3.2.1 Overlap

Initially the overlap between two gaussians is needed as it will be a recurring factor in the upcoming calculations. Again using the identity

(2.11) the overlap can be calculated directly.

$$\begin{aligned}
\langle A, \mathbf{s} | A', \mathbf{s}' \rangle &= \int \mathbf{d}^{3N} \mathbf{r} e^{-\mathbf{r}^T A \mathbf{r} + \mathbf{s}^T \mathbf{r}} e^{-\mathbf{r}^T A' \mathbf{r} + \mathbf{s}'^T \mathbf{r}} \\
&= \int \mathbf{d}^{3N} \mathbf{r} e^{-\mathbf{r}^T (A + A') \mathbf{r} + (\mathbf{s} + \mathbf{s}')^T \mathbf{r}} \\
&= \left(\frac{\pi^N}{\det(A + A')} \right)^{\frac{3}{2}} e^{\frac{1}{4} (\mathbf{s} + \mathbf{s}')^T (A + A')^{-1} (\mathbf{s} + \mathbf{s}')} \\
\langle A, \mathbf{s} | A', \mathbf{s}' \rangle &= \mathcal{M}(A + A', \mathbf{s} + \mathbf{s}') = \mathcal{M}(B, \mathbf{v}) \tag{3.6}
\end{aligned}$$

where $B = A + A'$ and $\mathbf{v} = \mathbf{s} + \mathbf{s}'$.

3.2.2 Kinetic energy

The classical kinetic energy is given by the kinetic energy operator which sums the energy contributions from the individual particles.

$$\hat{K} = - \sum_{i=1}^N \frac{\hbar^2}{2m_i} \frac{\partial^2}{\partial r_i^2} \tag{3.7}$$

More generally it can be written using introduced notation.

$$\hat{K} = - \frac{\partial}{\partial \mathbf{r}} \Lambda \frac{\partial}{\partial \mathbf{r}^T} \tag{3.8}$$

where Λ represents the constants. The matrix element for this operator can be evaluated using cumbersome integration and substitution and is given by [1].

$$\begin{aligned}
&\left\langle A, \mathbf{s} \left| - \frac{\partial}{\partial \mathbf{r}} \Lambda \frac{\partial}{\partial \mathbf{r}^T} \right| A', \mathbf{s}' \right\rangle \\
&= (6 \text{Tr}(A \Lambda A' B^{-1}) + (\mathbf{s} - 2A\mathbf{u})^T \Lambda (\mathbf{s}' - 2A'\mathbf{u})) \mathcal{M}(B, \mathbf{v}) \tag{3.9}
\end{aligned}$$

where $\mathbf{u} = \frac{1}{2} B^{-1} \mathbf{v}$ and Tr is the trace of the matrix

For the states with $\mathbf{s} = 0$ the matrix element simplifies.

$$\left\langle A \left| - \frac{\partial}{\partial \mathbf{r}} \Lambda \frac{\partial}{\partial \mathbf{r}^T} \right| A' \right\rangle = 6 \text{Tr}(A \Lambda A' B^{-1}) \mathcal{M}(B) \tag{3.10}$$

3.2.3 Coulomb potential

The coulomb potential using relative coordinates is equivalent to the electric potential that arises from a point charge [3].

$$V(r) = \frac{1}{4\pi\epsilon_0} \frac{Q}{r} \quad (3.11)$$

In the Hydrogen atom the charge will be equal to the e^2 and using electrostatic units the front factor can be completely omitted. To calculate the matrix element the following formula from [1] can be used:

$$\langle A, \mathbf{s} | f(|\mathbf{w}^T \mathbf{r}|) | A', \mathbf{s}' \rangle = \mathcal{M}(B, \mathbf{v}) \mathcal{J}[f] \quad (3.12)$$

where

$$\mathcal{J}[f] = \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} 2\pi \frac{e^{-\beta q^2}}{\beta q} \int_0^\infty r dr f(r) e^{-\beta r^2} \sinh(2\beta qr) \quad (3.13)$$

where $\beta = (\mathbf{w}^T B^{-1} \mathbf{w})^{-1}$ and $\mathbf{q} = \mathbf{w}^T \frac{1}{2} B^{-1} \mathbf{v}$.

For the coulomb potential with the form $\frac{1}{r}$ the element can be evaluated and the limit where \mathbf{s} , and therefore also \mathbf{q} , goes to zero can be found.

$$\left\langle A, \mathbf{s} \left| \frac{1}{|\mathbf{w}^T \mathbf{r}|} \right| A', \mathbf{s}' \right\rangle = \frac{\text{erf}(\sqrt{\beta} q)}{q} \xrightarrow{q \rightarrow 0} \frac{2\sqrt{\beta}}{\pi} \quad (3.14)$$

3.2.4 Harmonic oscillator potential

For model control the harmonic oscillator potential is also evaluated using an identical method to the coulomb potential. The general harmonic oscillator potential is given by:

$$V(r) = \frac{1}{2} m \omega^2 r^2 \quad (3.15)$$

This has the form of r^2 which can be used in (3.12) again.

$$\langle A, \mathbf{s} | |\mathbf{w}^T \mathbf{r}|^2 | A', \mathbf{s}' \rangle = \mathcal{M}(B, \mathbf{v}) \mathcal{J}[r^2] \quad (3.16)$$

$$= \mathcal{M}(B, \mathbf{v}) \left(\frac{\beta}{\pi}\right)^{\frac{3}{2}} 2\pi \frac{e^{-\beta q^2}}{\beta q} \int_0^\infty dr r^3 e^{-\beta r^2} \sinh(2\beta qr) \quad (3.17)$$

Now in the limit where q goes to zero this is easily evaluated:

$$\begin{aligned} \langle A, \mathbf{s} | |w^T \mathbf{r}|^2 | A', \mathbf{s}' \rangle &\xrightarrow{q \rightarrow 0} \mathcal{M}(B) \left(\frac{\beta}{\pi} \right)^{\frac{3}{2}} 4\pi \int_0^\infty dr r^4 e^{-\beta r^2} \\ &= \mathcal{M}(B) \left(\frac{\beta}{\pi} \right)^{\frac{3}{2}} 4\pi \frac{3\sqrt{\pi}}{8\beta^{5/2}} = \mathcal{M}(B) \frac{3}{2\beta} \end{aligned} \quad (3.18)$$

3.2.5 Relativistic kinetic energy

The relativistic kinetic energy operator is a differential operator in position space.

$$\hat{K}_{relativistic} = \sqrt{-\hbar^2 c^2 \frac{\partial^2}{\partial \mathbf{r}^2} + m^2 c^4} - mc^2 \quad (3.19)$$

In general differential operators are not a problem as long as they are raised to a whole number power. The square root in the relativistic energy however does not allow for this. The operator must be applied in momentum space using just the momentum.

$$\hat{K}_{relativistic} = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} - mc^2 \quad (3.20)$$

In momentum space the differential operator \hat{k} simply becomes a multiplicative operator which can be used by the formula (3.12) like before.

$$\langle A, \mathbf{s} | f(w^T \mathbf{k}) | A', \mathbf{s}' \rangle = \iint d^{3N} \mathbf{k} d^{3N} \mathbf{k}' \langle A, \mathbf{s} | \mathbf{k} \rangle \langle \mathbf{k} | f(w^T \mathbf{k}) | \mathbf{k}' \rangle \langle \mathbf{k}' | A', \mathbf{s}' \rangle \quad (3.21)$$

Now due to the normalization between the position and momentum overlap the integral is reduced and a factor is introduced. The gaussians are in the momentum form from (3.5):

$$\begin{aligned} &\langle A, \mathbf{s} | f(w^T \mathbf{k}) | A', \mathbf{s}' \rangle \\ &= \int \frac{d^{3N} \mathbf{k}}{(2\pi)^{3N}} \mathcal{M}(A, \mathbf{s}) \mathbf{g}_{\frac{1}{4}A^{-1}, -\frac{i}{2}A^{-1}\mathbf{s}}(\mathbf{k}) f(w^T \mathbf{k}) \mathcal{M}(A', \mathbf{s}') \mathbf{g}_{\frac{1}{4}A'^{-1}, -\frac{i}{2}A'^{-1}\mathbf{s}'}(\mathbf{k}) \end{aligned} \quad (3.22)$$

which reduces to the form of a matrix element:

$$= \frac{\mathcal{M}(A, \mathbf{s}) \mathcal{M}(A', \mathbf{s}')}{(2\pi)^{3N}} \left\langle \frac{1}{4}A^{-1}, -\frac{i}{2}A^{-1}\mathbf{s} \left| f(w^T \mathbf{k}) \right| \frac{1}{4}A'^{-1}, -\frac{i}{2}A'^{-1}\mathbf{s}' \right\rangle \quad (3.23)$$

Now finally applying (3.12) using (3.20) the following is found:

$$\begin{aligned} & \langle A, \mathbf{s} | \sqrt{(\hbar \mathbf{w}^T \mathbf{k})^2 c^2 + m^2 c^4} - mc^2 | A', \mathbf{s}' \rangle \\ &= \frac{\mathcal{M}(A, \mathbf{s}) \mathcal{M}(A', \mathbf{s}')}{(2\pi)^{3N}} \mathcal{M} \left(\frac{1}{4} (A^{-1} + A'^{-1}), -\frac{i}{2} (A^{-1} \mathbf{s} + A'^{-1} \mathbf{s}') \right) \mathcal{J}[f] \end{aligned} \quad (3.24)$$

Now again looking at the limit where q goes to zero the matrix element can be simplified.

$$\xrightarrow{q \rightarrow 0} \frac{\mathcal{M}(A) \mathcal{M}(A')}{(2\pi)^{3N}} \mathcal{M} \left(\frac{1}{4} (A^{-1} + A'^{-1}) \right) \left(\frac{\beta}{\pi} \right)^{\frac{3}{2}} 4\pi \int_0^\infty dr r^2 f(r) e^{-\beta r^2} \quad (3.25)$$

Now this is the end for the analytical part of the matrix element. A similar derivation is done in [5]. The final integral will be solved numerically during implementation.

3.2.6 Relativistic energy term using Taylor expansion

A somewhat easier way to determine the relativistic energy is from the Taylor expansion of the relativistic kinetic energy operator (3.20).

$$K_{rel} \approx \frac{\mathbf{p}^2}{2m} - \frac{\mathbf{p}^4}{8m^3 c^2} \dots \quad (3.26)$$

It is seen here that the initial term is the classical kinetic energy, which is expected since this is the physics in the low momentum limit. The second term however is a common approximation for the relativistic shift. Luckily the matrix element for this operator can be calculated fairly quickly in momentum space using the method of the previous section. To get the matrix element in the limit of q going to zero the form k^4 can be inserted directly into (3.25). This yields the following:

$$\begin{aligned} & \langle A | \mathbf{k}^4 | A' \rangle \\ &= \frac{\mathcal{M}(A) \mathcal{M}(A')}{(2\pi)^{3N}} \mathcal{M} \left(\frac{1}{4} (A^{-1} + A'^{-1}) \right) \left(\frac{\beta}{\pi} \right)^{\frac{3}{2}} 4\pi \int_0^\infty dr r^6 e^{-\beta r^2} \end{aligned} \quad (3.27)$$

$$= \frac{\mathcal{M}(A) \mathcal{M}(A')}{(2\pi)^{3N}} \mathcal{M} \left(\frac{1}{4} (A^{-1} + A'^{-1}) \right) \frac{15}{4\beta^2} \quad (3.28)$$

This matrix element is very useful as model control similar to the harmonic oscillator potential.

CHAPTER 4

Results

4.1 Implementation

4.1.1 Units

The matrix elements have been derived without explicit consideration for units and constants. As such it is necessary to compute the constants in the chosen units and apply the values when implementing the matrix elements. The units have been chosen such that the numbers can be calculated accurately within the double precision float point format which is used by python by default. Within this regime the units Ångstrom [\AA] and electronvolt [eV] have been chosen somewhat arbitrarily. Other common units in atomic physics include the Bohr radius [a_0] and Hartree [Ha].

The constants as used in the program are displayed in table 4.1:

$\hbar c$	1973.269 804 eV \AA
m_e	51 099.895 000 eV/c ²
m_p	938 272 088.16 eV/c ²
α	137.036 ⁻¹
a_0	0.529 177 210 903 \AA

TABLE 4.1: The exact numbers used in the implementation. The values are gathered online from NIST[6].

4.1.2 Program

The process of stochastic variation requires a random number generator for which the function `numpy.random.rand` from the `numpy` package for python is used. Here a random number between 0 and 1 is generated for each basis element and scaled by an appropriate factor and inversely squared to ensure an exponential like distribution of values.

Matrix elements are then found using the generated basis and the eigenstate is solved using `scipy.linalg.eigh` from the `scipy` package. This energy is then compared to the energies of previous states and the lowest energy state is selected and saved. After an arbitrary number of iterations the results can be examined and the relativistic corrections can be calculated from the low energy state given by both a basis and a state vector. For the relativistic matrix element the integral is evaluated numerically using `scipy.integrate.quad`.

Through approximate trial and error the configuration which found moderate success in convergence time was a scale value of 3 with 8 gaussians.

4.2 Classical Kinetic energy

4.2.1 Ground state energies

The targeted ground state energy with the coulomb potential can be calculated using the following from [4]:

$$E_1 = -\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = -13.605\,693\,1 \text{ eV} \quad (4.1)$$

however using the the reduced mass from the relative coordinates the value changes slightly

$$E_1 = -\frac{\mu_{ep}}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 = -13.598\,287 \text{ eV} \quad (4.2)$$

Both situations have been simulated and the lowest values from a few million stochastic trials are shown in table 4.2. The energies are quite

Reduced mass		Electron mass	
E	ΔE	E	ΔE
-13.597 08 eV	0.001206	-13.604 99 eV	0.000705

TABLE 4.2: Comparison of the lowest simulated energy using both the reduced mass and the regular electron mass. The ΔE denotes the difference with the masses from (4.1) and (4.2).

close to the analytic values, however for the reduced mass the result is only accurate down to 4 digits. This is worrying when considering that the relativistic shift to be calculated later is expected to lie in the 10^{-4} range. This will be discussed further in later sections.

4.2.2 Radial wave function

Using the basis and eigenvectors associated with the simulated ground state, it is possible to depict the radial wave function as seen in figure 4.1. The analytical ground state is depicted on top indicating that the simulated state fits the expected quite well, which is to be expected given that the energy difference is so low compared to the size of the wave function.

4.2.3 Harmonic oscillator potential

The ground state is also found in the harmonic oscillator potential. This is done primarily to check the model since the harmonic oscillator potential is expected to work very well with a gaussian basis. In fact the analytical solutions to the Hamiltonian with the harmonic oscillator is exactly a gaussian wave function. As expected the results match the ground state exactly down to the precision of python floating point. The ground state energy is $\frac{3}{2}\hbar\omega$ for the three dimensional harmonic oscillator.

4.3 Relativistic kinetic energy

The approximate expected value of the relativistic can be calculated using a perturbation as done in [4]. Using the reduced mass results in

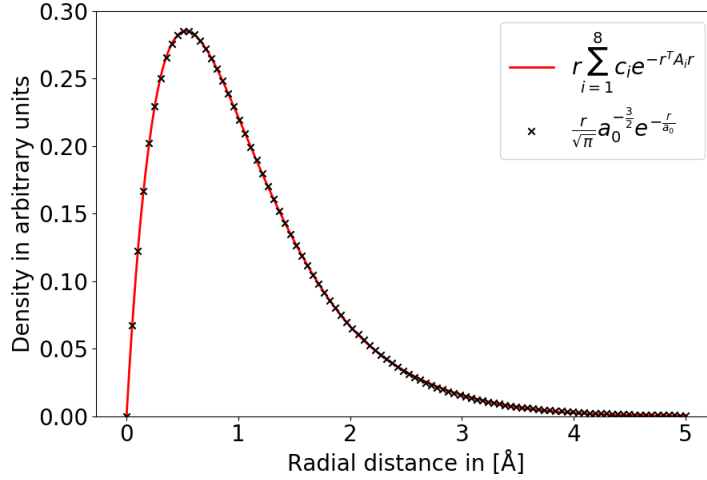


FIGURE 4.1: The simulated wave function is depicted on top of the theoretical normalized ground state wave function.

the following value:

$$E_{rel}^{(1)} = -\frac{5(E_1)^2}{2\mu_{ep}c^2} = -9.05159 \times 10^{-4} \text{ eV} \quad (4.3)$$

AS previously mentioned the energy of the simulated ground state is quite far off the perturbation energy, relative to the expected relativistic shift, which could mean that the relativistic energy difference would be lost. To investigate this, a large amount of simulations with different amounts of trials have been carried out inspired by resampling methods from statistics. By making grouped simulations with either 10000 trials or 500000 trials it was possible to determine whether information about the relativistic shift is still present without being within the effect size of the true energy. A visual examination of this can be seen in figure 4.2. Here it is seen, within some uncertainty, that simulations with more or less accurate classical ground states still find a similar relativistic shift. These simulations were also calculated for the Taylor approximation of the relativistic shift. This is seen in table 4.3.

In both models the relativistic shift settles somewhat consistently to a value without an unreasonable uncertainty, as estimated by the

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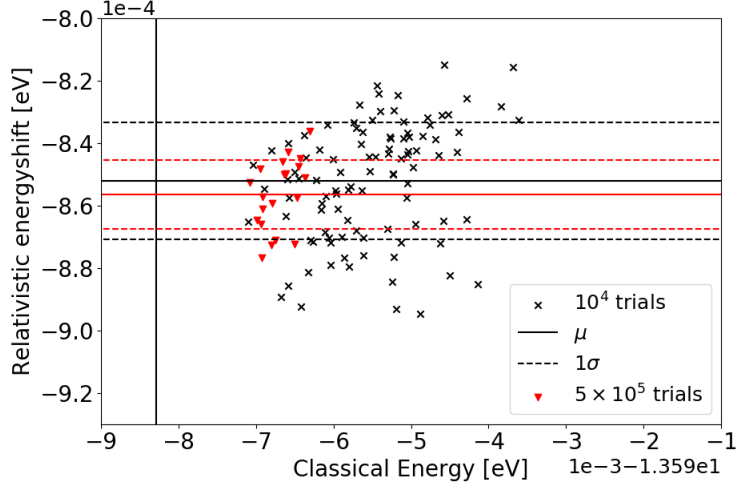


FIGURE 4.2: The two groups of 10^4 trials and 5×10^5 trials with the sample mean and the sample standard deviation. The vertical line denotes the analytic classical ground state energy.

	Full model		Taylor Approximation	
	10^5 trials	5×10^5 trials	10^5 trials	5×10^5 trials
μ	-8.521×10^{-4}	-8.564×10^{-4}	-8.540×10^{-4}	-8.582×10^{-4}
σ	1.874×10^{-5}	1.108×10^{-5}	1.977×10^{-5}	1.158×10^{-5}

TABLE 4.3: The table displays the sample mean and sample standard deviation for the 10^4 group and the 5×10^5 group in both the full model using the numerically calculated matrix element and in the Taylor approximation model.

sample standard deviation. The group with the more accurate classical energy however has a somewhat greater shift which could indicate that the true shift is even lower. This would be consistent with the analytical calculation of the Taylor approximation which landed on a value about 5×10^{-5} lower than what was found. It is possible that through more simulations a group of data could be used to extrapolate into the energy range where the classical approximation is better and find a relativistic shift closer to the perturbation calculation. Especially for the data gathered in the Taylor model. It is also important to note however that adding further terms to the Taylor expansion will also

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affect the result. Ultimately the simulated method is comparable to a simple perturbation calculation and even for a less accurate ground state, the method will give an arguably useful estimate of the shift.

CHAPTER 5

Conclusion

The hydrogen atom has been examined using a correlated gaussian basis whose matrix elements have been developed. Through complete stochastic variation the ground state of the system has been found within 0.000 705 eV of the analytical ground state. Despite this not being within the 10^4 digit range, the simulation of the relativistic shift has been carried out. Using methods inspired by statistical resampling, the relativistic shift has been estimated to -8.564×10^{-4} eV which is quite close to the value of $-9.051 59 \times 10^{-4}$ eV as estimated by a perturbation calculation. Through statistical extrapolation it might be possible to get a value even closer. Ultimately stochastic variation with correlated gaussians was found to be a comparable method to perturbation calculations and even giving a good estimate despite being far away from the ground state energy which could be useful for systems where the ground state is harder to approach.

Bibliography

- [1] D. V. Fedorov. ‘Analytic Matrix Elements and Gradients with Shifted Correlated Gaussians’. In: *Few-Body Systems* 58.1 (Dec. 2016).
- [2] D. V. Fedorov. ‘A Nuclear Model with Explicit Mesons’. In: *Few-Body Systems* 61.4 (Oct. 2020).
- [3] David J. Griffiths. *Introduction to electrodynamics*. fourth Edition. Cambridge, 2017.
- [4] David J. Griffiths and Darrel F. Schroeter. *Introduction to Quantum Mechanics*. Third Edition. Cambridge, 2018.
- [5] Yasuyuki Suzuki and Kálmán Varrga. *Stochastic Variational Approach to Quantum-Mechanical Few-Body Problems*. First Edition. Lecture Notes in Physics Monographs. Springer Berlin, Heidelberg, 2013.
- [6] Eite Tiesinga et al. ‘CODATA Recommended Values of the Fundamental Physical Constants: 2018’. en. In: 93 (2021-06-30 04:06:00 2021).