ON COMPUTING BOUND STATES OF THE DIRAC AND SCHröDINGER EQUATIONS

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ABSTRACT. We cast the quantum chemistry problem of computing bound states as that of solving a set of auxiliary eigenvalue problems for a family of parameterized compact integral operators. The compactness of operators assures that their spectrum is discrete and bounded with the only possible accumulation point at zero. We show that, by changing the parameter, we can always find the bound states, i.e., the eigenfunctions that satisfy the original equations and are normalizable. While for the non-relativistic equations these properties may not be surprising, it is remarkable that the same holds for the relativistic equations where the spectrum of the original relativistic operators does not have a lower bound. We demonstrate that starting from an arbitrary initialization of the iteration leads to the solution, as dictated by the properties of compact operators.

1. INTRODUCTION

We develop, analyze, and demonstrate a method for computing bound states for both the non-relativistic Schrödinger and relativistic Dirac equations of quantum chemistry (QC). As is well-known, the equations of quantum mechanics allow both bound and scattering states; inter alia this implies that, if the scattering states are present, then it is impossible to construct a single self-adjoint operator that would have only the bound states since the resulting basis of eigenvectors would be incomplete. We show that, instead, there is an auxiliary one parameter family of compact operators such that the sought bound states are found by computing eigenfunctions of particular members of this family. In fact, this family of operators constructed using a parameterized Green’s function and yielding (what we call) the integral form of the Schrödinger equation is well-known as it has been used in mathematical analysis since 1950s. It has long been established that, for certain classes of potentials and for the parameter corresponding to the bound states, the relevant operators are compact. A particularly important for QC problems is the Rollnik class of potentials arrived at and analyzed by several authors, see [17, 19, 7, 8, 18, 20, 21] and references therein. We elaborate on this later in the paper.

The early use of the integral form of the Schrödinger equation for computational purposes was pioneered by Kalos using Monte-Carlo approach [11] and, more recently, employed in adaptive multiresolution QC algorithms in [10, 2] (see also [2] and references therein). In this paper we revisit our approach for computing bound states by solving the integral form of the Dirac equations of QC in [2] (and that of the non-relativistic equations in [10]) to demonstrate that convergence interpreted in these papers as being local (thus requiring an initial guess sufficiently close to the desired bound state eigenfunction) is, in
fact, a robust global convergence. We demonstrate this by showing that relevant operators are compact.

The integral form of the Schrödinger equation is obtained using a parameterized Green’s function yielding an auxiliary family of integral operators. The parameter can be tuned and, at certain discrete values, the corresponding operator yields the desired bound states. This approach found its application in an adaptive multiresolution method for solving non-relativistic equations of QC for computing bound states introduced in [10] and implemented in MADNESS (Multiresolution ADaptive Numerical Environment for Scientific Simulation, see [9]). We note that since the spectrum of non-relativistic Hamiltonians of QC is bounded from below, it is not surprising that the spectra of all operators of the auxiliary family of integral operators are also bounded from below as they turn out to be compact operators for all values of the parameter. While it may appear that using a family of integral operators instead of the single Hamiltonian is computationally more expensive, the separated multiresolution representation of operators in [10] actually makes MADNESS a fast method for accurate computations in QC and nuclear sciences [9].

Turning to the relativistic equations, it is well-known that the spectrum of the Dirac Hamiltonian is not bounded from below so that the problem of finding bound states can not be cast as that of minimization of a quadratic form, the so-called Rayleigh quotient. As a consequence, computing bound states by directly discretizing the relativistic Hamiltonian requires additional numerical devices to guide computation to the desired bound states. Thus, it is remarkable that for relativistic equations of QC the associated auxiliary family of integral operators consists of compact operators as long as the parameter — the relativistic energy — is selected to be positive. We show that, by selecting the positive relativistic energy, the equations yield only the desired bound states so that there is no need to numerically exclude either the positive-energy scattering states or all negative-energy states.

The integral form of the Dirac Hamiltonian was proposed in [4] and used in [2] for computing relativistic energies of bound states. In that context, we had originally interpreted convergence of the integral iteration as being local — i.e., requiring an initial guess sufficiently close to the desired bound state eigenfunction. Instead, in this paper we demonstrate, both theoretically and numerically, robust global convergence to the sought bound state. We cast the iteration that yields the desired bound states as a combination of the power method and the Newton’s method, which allows us to demonstrate that we can always find an appropriate member of the family of integral operators in order to solve the original problem of finding a bound state. Some of the proofs needed in the main text can be found in Appendices 8.1-8.4.
2. Integral Form of Equations of Quantum Chemistry

We use examples of the one-electron Kohn-Sham [16] equations and their relativistic counterparts in Dirac’s formulation with the point-charge Coulomb potential [14] to motivate and demonstrate our approach. Methods of quantum chemistry differ in how they replace the electron-electron interaction by the interaction of an electron with an averaged field generated by all electrons; however the singular part of the total potential, the Coulomb electron-nuclear interaction, is the same in most methods [14, 15]. The singularity does not arise if a finite-size model is adopted for the nuclear charge distribution [22] instead of the idealized point-charge model, although any smoothing only occurs within the radius of the nuclear charge distribution that is $O(10^{-5})$ smaller than the radius of the atomic charge distribution. Relativistic pseudo-potentials [5] further smooth the potential and also eliminate the most tightly-bound (i.e., core) electrons that experience the strongest relativistic effects. However, all-electron calculations with both point and finite nuclear models are still essential in order to directly access the properties of core electrons in molecular environments, to employ general relativistic Hamiltonians, and to eliminate/assess the approximations inherent to pseudo-potentials. In demonstrating compactness of a family of integral operators, the Coulomb electron-nuclear interaction presents the main obstacle and, for this reason, we can limit our discussion to these two examples of QC equations.

2.1. The Kohn-Sham equations. Consider occupied orbitals $\psi_i(r), i = 1, \ldots, N$ defining the electron density

$$\rho(r) = 2 \sum_{i=1}^{N} |\psi_i(r)|^2,$$

which are the lowest $N$ eigenfunctions of the Kohn-Sham operator

$$\left(-\frac{1}{2} \Delta + V(r)\right) \psi_i(r) = E_i \psi_i(r), \ i = 1, \ldots, N,$$

where

$$V(r) = V_{ext}(r) + V_c(r) + V_{xc}(r).$$

For molecules, the external potential includes the attraction of the electrons to the nuclei,

$$V_{ext}(r) = -\sum_{\alpha} \frac{Z_{\alpha}}{\|r - R_{\alpha}\|},$$

($Z_{\alpha}$ and $R_{\alpha}$ being the nuclear charge and position, respectively). The Coulomb potential describes the repulsion between electrons,

$$V_c(r) = \int_{\mathbb{R}^3} \frac{\rho(r')}{\|r - r'\|} dr'$$

and the exchange-correlation potential $V_{xc}$ that in this work is taken to be a scalar that within the generalized gradient approximation (GGA) depends on $\rho$ and its derivatives at that point. Non-local potentials, such as the Hartree-Fock exchange potential [16], can be included as well. The Hartree-Fock exchange potential has singularities at locations of nuclei (e.g. cusps in the non-relativistic case), but these singularities are necessarily weaker than those of the external potential $V_{ext}$ at the same locations. Our estimates depend only on the slowest decay exhibited by the total potential in momentum space, which are due to the stronger singularity of $V_{ext}$. 
Introducing the Green’s function

\[ (-\Delta + \mu^2) G_{\mu} (\mathbf{r}, \mathbf{r}') = \delta (\mathbf{r} - \mathbf{r}'), \quad G_{\mu} (\mathbf{r}, \mathbf{r}') = \frac{e^{-\mu |\mathbf{r} - \mathbf{r}'|}}{4\pi |\mathbf{r} - \mathbf{r}'|}, \]

we consider the auxiliary coupled eigenvalue problems

\[ \lambda_\mu \psi_\mu = -2G_{\mu} V \psi_\mu, \quad i = 1, \ldots, N. \]

If \( \mu_i^2 = -2E_i \), then \( \lambda_\mu = 1 \) and functions \( \psi_\mu \) also solve (2.1). Introducing functions

\[ \phi_\mu = G_{\mu}^{-1/2} \psi_\mu, \]

the auxiliary eigenvalue problem (2.5) becomes

\[ \lambda_\mu \phi_\mu = -2G_{\mu}^{1/2} V G_{\mu}^{1/2} \phi_\mu, \quad i = 1, \ldots, N. \]

In what follows, we consider operators \( V G_{\mu}^{1/2} \) and show that, by choosing an appropriate Hilbert space for the solutions (2.5), these operators are compact.

Remark 1. In the analysis that follows, we want the potential \( V \) in (2.5) (and therefore in (2.6)) to be a negative definite multiplication operator. While \( V_{\text{ext}} \) is negative, the additional components of the total potential, \( V_c (\mathbf{r}) \) and \( V_{\text{sc}} (\mathbf{r}) \), may possibly violate this property of \( V \) in some subdomains. In such case, as long as \( V_c (\mathbf{r}) \) and \( V_{\text{sc}} (\mathbf{r}) \) are bounded, we can modify the derivation of (2.5) and (2.6) by first shifting the spectrum

\[ \left( -\frac{1}{2} \Delta + V (\mathbf{r}) - \tau \right) \psi_i (\mathbf{r}) = (E_i - \tau) \psi_i (\mathbf{r}), \quad i = 1, \ldots, N, \]

where \( \tau > 0 \) is a sufficiently large shift so that

\[ V (\mathbf{r}) - \tau < 0, \]

and considering

\[ \lambda_\mu \psi_\mu = -2G_{\mu} (V - \tau) \psi_\mu. \]

While the shifted potential is not zero at infinity, for as long as the eigenfunctions \( \psi_\mu \) of (2.1) decay exponentially (as it is the case for the Schrödinger equation, see [1]), the integrals in (2.8) are well defined. In fact, in solving (2.1) numerically, the functions \( \psi_\mu \) are considered to be non-zero only in a bounded domain. In (2.8), if \( \mu_i^2 = -2(E_i - \tau) \), then \( \lambda_\mu = 1 \) and functions \( \psi_\mu \) also solve (2.1). So far in our computations we did not encounter a need to shift the spectrum. However, without loss of generality, it is important to consider \( V \) to be a negative definite multiplication operator.

2.2. Integral form of Dirac’s equations. An orbital (one-particle eigenfunction) of the relativistic Dirac equations is a four-component vector-function (i.e., a spinor) \( \psi \) which satisfies

\[ \mathcal{H} \psi = E \psi \]

where

\[ \mathcal{H} = \mathcal{H}_0 + \mathcal{V} (\mathbf{r}), \]

\[ \mathcal{H}_0 = \frac{\hbar c}{i} \left( \alpha_1 \frac{\partial}{\partial x_1} + \alpha_2 \frac{\partial}{\partial x_2} + \alpha_3 \frac{\partial}{\partial x_3} \right) + \beta mc^2, \]

\[ \alpha_1 = \begin{pmatrix} 0 & \sigma_1 & 0 \\ \sigma_1 & 0 & 0 \end{pmatrix}, \quad \alpha_2 = \begin{pmatrix} 0 & \sigma_2 & 0 \\ \sigma_2 & 0 & 0 \end{pmatrix}, \quad \alpha_3 = \begin{pmatrix} 0 & \sigma_3 & 0 \\ \sigma_3 & 0 & 0 \end{pmatrix} \]

and

\[ \beta = \begin{pmatrix} \sigma_0 & 0 \\ 0 & -\sigma_0 \end{pmatrix}, \]
Therefore, we have
\[ \sigma_0 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \]
are the Pauli matrices such that
\[ \sigma_1^2 = \sigma_2^2 = \sigma_3^2 = \sigma_0, \]
and
\[ \sigma_1 \sigma_2 = i \sigma_3, \quad \sigma_2 \sigma_3 = i \sigma_1, \quad \sigma_3 \sigma_1 = i \sigma_2. \]
The matrix-potential operator is
\[ \mathcal{V}'(\mathbf{r}) = \begin{pmatrix} V & 0 & 0 & 0 \\ 0 & V & 0 & 0 \\ 0 & 0 & V & 0 \\ 0 & 0 & 0 & V \end{pmatrix}, \]
where the potential \( V \) has several components as in (2.2). As in the non-relativistic case, we can consider a system of equations involving \( N \) orbitals where the electron-electron interactions are captured as an interaction of an electron with an averaged potential generated by all electrons. As in the non-relativistic Kohn-Sham equations, we can assign the four-component orbitals to each electron and consider a system of coupled eigenvalue problems. Avoiding complicating notations, without loss of generality, we only consider operators that involve a single orbital.

Setting
\[ \mathcal{J} = \begin{pmatrix} \sigma_0 & 0 \\ 0 & \sigma_0 \end{pmatrix}, \]
we rewrite (2.9) as
\[ (\mathcal{H}_0 - E\mathcal{J}) \psi = -\mathcal{V}'(\mathbf{r}) \psi, \]
where
\[ \mathcal{H}_0 - E\mathcal{J} = \frac{\hbar c}{i} \left( \sigma_1 \frac{\partial}{\partial x_1} + \sigma_2 \frac{\partial}{\partial x_2} + \sigma_3 \frac{\partial}{\partial x_3} \right) + \mathcal{J}_0 mc^2 - E\mathcal{J}. \]
Following (4) and computing
\[ (\mathcal{H}_0 - E\mathcal{J}) (\mathcal{H}_0 + E\mathcal{J}) = \mathcal{H}_0^2 - E^2 \mathcal{J}, \]
we have on the off-diagonal of \( \mathcal{H}_0^2 \)
\[ \sigma_0 mc^2 \frac{\hbar c}{i} \left( \sigma_1 \frac{\partial}{\partial x_1} + \sigma_2 \frac{\partial}{\partial x_2} + \sigma_3 \frac{\partial}{\partial x_3} \right) - \frac{\hbar c}{i} \left( \sigma_1 \frac{\partial}{\partial x_1} + \sigma_2 \frac{\partial}{\partial x_2} + \sigma_3 \frac{\partial}{\partial x_3} \right) \sigma_0 mc^2 = 0 \]
and on the diagonal
\[ \sigma_0 m^2 c^4 - \hbar^2 c^2 \left( \sigma_1 \frac{\partial}{\partial x_1} + \sigma_2 \frac{\partial}{\partial x_2} + \sigma_3 \frac{\partial}{\partial x_3} \right)^2 = \sigma_0 \left( m^2 c^4 - \hbar^2 c^2 \Delta \right). \]
Therefore, we have
\[ \mathcal{H}_0^2 - E^2 \mathcal{J} = \mathcal{J} \left( m^2 c^4 - \hbar^2 c^2 \Delta - E^2 \right) \]
and
\[ (\mathcal{H}_0 + E\mathcal{J})^{-1} (\mathcal{H}_0 - E\mathcal{J})^{-1} = (\mathcal{H}_0^2 - E^2 \mathcal{J})^{-1} = \mathcal{J} \left( -\hbar^2 c^2 \Delta + m^2 c^4 - E^2 \right)^{-1} \]
so that
\[ (\mathcal{H}_0 - E\mathcal{J})^{-1} = (\mathcal{H}_0 + E\mathcal{J}) \mathcal{J} \left( -\hbar^2 c^2 \Delta + m^2 c^4 - E^2 \right)^{-1}. \]
As a result, we obtain from (2.12)
\[ \psi = \frac{-1}{\bar{\hbar}^2 c^2} (H_0 + E \mathcal{I})^{-1} \mathcal{J} (\Delta + \frac{m^2 c^4 - E^2}{c^2 \bar{\hbar}^2})^{-1} \mathcal{J}^* \psi. \]

Noting that for bound states \( E < mc^2 \), we set
\[ (2.13) \quad \kappa = \frac{\sqrt{m^2 c^4 - E^2}}{\bar{\hbar}}, \quad \kappa > 0, \]
and
\[ (2.14) \quad \left( -\Delta + \frac{m^2 c^4 - E^2}{c^2 \bar{\hbar}^2} \right)^{-1} (\mathbf{r} - \mathbf{r}') = G(\kappa, \mathbf{r} - \mathbf{r}') = \frac{1}{4\pi} \frac{e^{-\kappa \| \mathbf{r} - \mathbf{r}' \|}}{\| \mathbf{r} - \mathbf{r}' \|}. \]

where the Green’s function (2.14) solves
\[ (2.15) \quad (\Delta + \kappa^2) G(\kappa, \mathbf{r} - \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r')} . \]

We consider an auxiliary eigenvalue problem
\[ (2.16) \quad \lambda(\kappa) \psi(\kappa) = \frac{-1}{\bar{\hbar}^2 c^2} (H_0 + E(\kappa) \mathcal{I}) G(\kappa) V \psi(\kappa), \]
where
\[ (2.17) \quad G(\kappa, \mathbf{r} - \mathbf{r}') = \mathcal{J} G(\kappa, \mathbf{r} - \mathbf{r}'). \]

Note that if \( \kappa \) is as in (2.13), where \( E \) is an eigenvalue of (2.9), then \( \lambda(\kappa) = 1 \) and the solution of (2.16) \( \psi(\kappa) \) also solves (2.9). It is convenient to introduce a four component function \( \Phi(\kappa) = G^{-1/2}(\kappa) \psi(\kappa) \) to modify (2.16) so that
\[ (2.18) \quad \lambda(\kappa) \Phi(\kappa) = \mathcal{A}(\kappa) \Phi(\kappa), \]
where
\[ (2.19) \quad \mathcal{A}(\kappa) = -\frac{1}{\bar{\hbar}^2 c^2} (H_0 + E(\kappa) \mathcal{I}) G^{1/2}(\kappa) V G^{1/2}(\kappa). \]

We show further below that, in the appropriately chosen Hilbert spaces, the operator
\[ \mathcal{A}(\kappa) \]

is bounded, the operator
\[ \mathcal{J} G^{1/2}(\kappa) \]

is compact, and the spectrum of the operator \( \mathcal{A} \) is real.

**Remark 2.** As in the non-relativistic case (see Remark (1)), we want the matrix potential \( V \) in (2.11) to be negative definite. Assuming that \( V_{\mathbf{c}}(\mathbf{r}) \) and \( V_{\mathbf{m}}(\mathbf{r}) \) are bounded and using an appropriate shift \( \tau \) of the spectrum in our derivation of (2.16) and (2.18), we write
\[ (2.20) \quad (H_0 + V(\mathbf{r}) - \tau \mathcal{I}) \psi = (E - \tau) \psi, \]
where \( \tau \) is sufficiently large. In such case \( E - \tau < E < mc^2 \) and we set
\[ (2.21) \quad \kappa = \frac{\sqrt{m^2 c^4 - (E - \tau)^2}}{c \bar{\hbar}}, \quad \kappa > 0. \]

We then have
\[ (2.22) \quad \mathcal{A}(\kappa) = -\frac{1}{\bar{\hbar}^2 c^2} (H_0 + E(\kappa) \mathcal{I}) G^{1/2}(\kappa) (V - \tau \mathcal{I}) G^{1/2}(\kappa). \]
As in the non-relativistic case, components of $\phi$ in (2.18) are computationally considered to be non-zero in a bounded domain. Again, so far in our computations we did not encounter a need to shift the spectrum. The shift of the spectrum (if it were needed) allows us to consider $\mathcal{Y}$ to be a negative definite matrix multiplication operator without loss of generality.

3. HILBERT SPACES FOR SOLUTIONS OF EQUATIONS OF QUANTUM CHEMISTRY

For our analysis it is convenient to consider equations of quantum chemistry in momentum space, where the Green’s function component in (2.17) is

$$G(\kappa, \|p\|) = \left( \kappa^2 + \|p\|^2 \right)^{-1}.$$

If $\hat{\psi}(p)$ is a component of the spinor solution of the Dirac equation, we require

$$\hat{\phi}(p) = \left( \kappa^2 + \|p\|^2 \right)^{1/2+\delta/2} \hat{\psi}(p) \in L^2(\mathbb{R}^3),$$

where $\kappa > 0$ and $\delta > 0$, i.e. the function $\psi$ belongs to the Hilbert space $\mathcal{H}_\kappa,\delta$ with the weighted inner product

$$(\psi_1, \psi_2)_{\kappa,\delta} = \int_{\mathbb{R}^3} \left( \kappa^2 + \|p\|^2 \right)^{1+\delta} \hat{\psi}_1(p) \overline{\hat{\psi}_2(p)} dp$$

and the corresponding norm,

$$\|\psi\|_{\kappa,\delta} = \left( \int_{\mathbb{R}^3} \left( \kappa^2 + \|p\|^2 \right)^{1+\delta} |\hat{\psi}(p)|^2 dp \right)^{1/2}.$$ 

For non-relativistic equations this condition (for $\hat{\psi}_\mu(p)$ in (2.5)) is easily satisfied since the worst singularity of a solution is a cusp at the location of a nuclei, e.g. $e^{-\|r\|}$, which in momentum space corresponds to $\left( 1 + \|p\|^2 \right)^{-2}$. Consequently, for large $\|p\|$, the asymptotic rate of decay of non-relativistic bound states in momentum space is $\|p\|^{-4}$ which is sufficient to keep the integral in (3.2) finite. Note that the eigenfunctions with a polynomial factor that is zero at the origin decay even faster in momentum space.

The solutions of Dirac’s equation have a stronger singularity at the location of a nuclei, e.g.

$$\|r\|^{-\gamma(Z)-1} e^{-\|r\|},$$

with

$$\gamma(Z) = \left( 1 - \left( \frac{Z}{c} \right)^2 \right)^{1/2}, \quad 0 < \gamma(Z) < 1,$$

where $Z$ is the charge of the nucleus and $c$ is the speed of light, $c \approx 137.035999084$ in atomic units (see e.g. \[13\] Section 2.3), \[12\] Section 3.1). Note that to estimate the decay we cannot use a stronger singularity $\|r\|^{-1} e^{-\|r\|}$ instead of (3.3) since, in momentum space, it corresponds to $\left( 1 + \|p\|^2 \right)^{-1}$ and this rate of decay is too slow to keep (3.2) finite. Therefore, we need to estimate the rate of decay of solutions of Dirac’s equations in momentum space for (3.3) directly. Computing the Fourier transform of (3.3), we obtain (see
ψ_0(p) = \int_{\mathbb{R}^3} |r|^{\gamma(Z)-1} e^{-|r|} e^{-i r \cdot p} dr
= \frac{4\pi}{p} \int_0^\infty e^{-r} r^{\gamma(Z)} \sin(pr) dr
= \frac{4\pi \Gamma(1 + \gamma(Z)) \sin \left[ (1 + \gamma(Z)) \arctan(p) \right]}{p (1 + p^2)^{1/2 + \gamma(Z)/2}}
= \frac{4\pi \Gamma(1 + \gamma(Z)) \sin \left[ \frac{1}{2}(1 + \gamma(Z)) \pi \right]}{p (1 + p^2)^{1/2 + \gamma(Z)/2}} + O \left( \frac{1}{p^{3+\gamma(Z)}} \right),

where r = |r| and p = |p|. Since \gamma(Z) < 1 and for large p
\sin \left[ (1 + \gamma(Z)) \arctan(p) \right] = \sin \left[ \frac{1}{2}(1 + \gamma(Z)) \pi \right] - \frac{1}{p} (1 + \gamma(Z)) \cos \left[ \frac{1}{2}(1 + \gamma(Z)) \pi \right] + O \left( \frac{1}{p^2} \right),
we obtain
ψ_0(p) = \frac{4\pi \Gamma(1 + \gamma(Z)) \sin \left[ \frac{1}{2}(1 + \gamma(Z)) \pi \right]}{p (1 + p^2)^{1/2 + \gamma(Z)/2}} + O \left( \frac{1}{p^{3+\gamma(Z)}} \right).

Estimating the norm (3.2), we observe that the integrand in (3.2) behaves as
\frac{1}{p^{2+2\gamma(Z)-2\delta}}
for large p. For convergence we need 2 + 2\gamma(Z) - 2\delta > 3 or
\gamma(Z) > \frac{1}{2} + \delta.

Since \gamma(Z) is a monotone function and \gamma(118) = 0.508457, we conclude that, for a sufficiently small \delta > 0, we can use the Hilbert space \mathcal{H}_{\kappa,\delta} with the weighted inner product (3.1) as a space for the bound states of the Dirac’s equations for nuclei with charges 1 ≤ Z ≤ 118.

Our interest in considering the Hilbert space \mathcal{H}_{\kappa,\delta} is more theoretical than practical. In all practical computations the singularity of the nuclear potentials is removed either explicitly or implicitly as a result of either using a finite computational basis or grid or through the use of a more physical finite charge distribution of the nucleus. As we discuss next, if we consider solutions in \mathcal{H}_{\kappa,0} (i.e. set \delta = 0 in (3.1)), then the operators we construct are compact for an arbitrarily accurate approximation of the Coulomb potential for any nuclei charge Z < c. It turns out that by considering solutions in \mathcal{H}_{\kappa,\delta}, for nuclei charges 1 ≤ Z ≤ 118 the operators in question are compact for the Coulomb potential itself, without any approximation. In any case, the practical impact of our considerations is that the spectrum of the family of operators of the auxiliary eigenvalue problems (2.6) and (2.18) is always discrete and bounded from below which, in turn, assures convergence of an iterative approach for computing the bound states.

4. The Hilbert-Schmidt operators

We start by considering the matrix operator \mathcal{A}^{1/2} which, in the momentum space, can be written as
(4.1) \left[ \mathcal{A}^{1/2} \right](\kappa, p, p') = \mathcal{A} \frac{\vec{V}(p - p')}{(\kappa^2 + ||p'||^2)^{1/2}},
acting on functions
\[ \hat{\varphi}(\mathbf{p}) = \left( \kappa^2 + \|\mathbf{p}\|^2 \right)^{1/2} \hat{\psi}(\mathbf{p}) \in L^2(\mathbb{R}^3), \]
or \( \psi \in \mathcal{H}_{\kappa,0} \). Alternatively, we can consider the matrix operator
\[
(4.2) \quad \left[ \gamma^\alpha \gamma^1 / 2 \right]_{\delta} (\kappa, \mathbf{p}, \mathbf{p}') = \left( \kappa^2 + \|\mathbf{p}'\|^2 \right)^{1/2} \hat{V}(\mathbf{p} - \mathbf{p}'),
\]
acting on functions
\[ \hat{\varphi}(\mathbf{p}) = \left( \kappa^2 + \|\mathbf{p}\|^2 \right)^{1/2} \hat{\psi}(\mathbf{p}) \in L^2(\mathbb{R}^3), \]
or \( \psi \in \mathcal{H}_{\kappa,\delta} \), a class of functions \( \psi \) decaying slightly faster in the momentum space.

Combining these operators with their Hermitian adjoints which we denote by \( * \), we obtain
\[
\left[ \gamma^\alpha \gamma^1 / 2 \right] \left[ \gamma^\alpha \gamma^1 / 2 \right]^* = \gamma^1 / 2 \gamma^2 \gamma^1 / 2
\]
and
\[
\left[ \gamma^\alpha \gamma^1 / 2 \right]^* \left[ \gamma^\alpha \gamma^1 / 2 \right] = \gamma^1 / 2 \gamma^2 \gamma^1 / 2.
\]

Our goal is to show that the matrix operators \( \gamma^\alpha \gamma^1 / 2 \) and \( \gamma^1 / 2 \gamma^2 \gamma^1 / 2 \) are compact; for this we rely on Lemma 7 (see Appendix 8.1) showing that the compactness of operators \( \gamma^1 / 2 \gamma^2 \gamma^1 / 2 \) (or \( \gamma^1 / 2 \gamma^2 \gamma^1 / 2 \)) implies compactness of \( \left[ \gamma^\alpha \gamma^1 / 2 \right] \) (or \( \left[ \gamma^\alpha \gamma^1 / 2 \right] \)), respectively.

We study components of these matrix operators
\[ G^{1/2} V^2 G^{1/2}, \]
and
\[ G_{\delta}^{1/2} V^2 G_{\delta}^{1/2}, \]
which have the kernels
\[
(4.3) \quad K(\kappa, \mathbf{p}, \mathbf{p}') = \frac{\hat{V}^2(\mathbf{p} - \mathbf{p}')}{{\left( \kappa^2 + \|\mathbf{p}\|^2 \right)}^{1/2} \left( \kappa^2 + \|\mathbf{p}'\|^2 \right)^{1/2}}
\]
and
\[
(4.4) \quad K_{\delta}(\kappa, \mathbf{p}, \mathbf{p}') = \frac{\hat{V}^2(\mathbf{p} - \mathbf{p}')}{{\left( \kappa^2 + \|\mathbf{p}\|^2 \right)}^{1+\delta/2} \left( \kappa^2 + \|\mathbf{p}'\|^2 \right)^{1+\delta/2}}.
\]

4.1. The Rollnik class of potentials. We have

**Theorem 3.** ([20, Theorem I.22]) *If potential \( V^2 \) is in the Rollnik class, then the operator \( G^{1/2} V^2 G^{1/2} \) with the kernel \( K(\kappa, \mathbf{p}, \mathbf{p}') \) is a bounded Hilbert-Schmidt operator.*

In other words, if the potential \( V^2 \) is in the Rollnik class, then the integral
\[
(4.5) \quad \|K\|_{HS} = \left( \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{\left| \hat{V}^2(\mathbf{p} - \mathbf{p}') \right|^2}{{\left( \kappa^2 + \|\mathbf{p}\|^2 \right)}^{1/2} \left( \kappa^2 + \|\mathbf{p}'\|^2 \right)^{1/2}} d\mathbf{p}' d\mathbf{p} \right)^{1/2}
\]
is finite. It is well known that the Hilbert-Schmidt operators are compact.
The Rollnik class of potentials is defined by the condition (see [20])
\[ \int_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{|V(r)||V(r')|}{||r-r'||^2} drdr' < \infty, \]
which can be shown to be equivalent to (4.5) (see [20] Theorem I.22). Note that in our case it is a requirement for \( V^2 \) rather than \( V \). The Rollnik class of potentials has been identified independently by a number of authors [17, 19, 7, 8, 18] as a class of physically significant potentials that have workable mathematical properties. Quoting from [19, page 126]: "The latter quantity exists for potentials that decrease more rapidly than \( ||r||^{-2} \) as \( ||r|| \to \infty \) and that in the neighborhoods of a finite number of points \( r_0 \) are less singular than \( ||r-r_0||^{-2\alpha} \). Note that since we consider the square of the potential in Theorem 3 for the Coulomb potential we are just at the threshold of missing the Rollnik class.

In practical computation we replace the Coulomb potential by a linear combination of Gaussians. Following [3, Theorem 5 and Lemma 4] and setting
\[ S_\infty (||r||) = \frac{h}{\Gamma(\alpha/2)} \sum_{n \in \mathbb{Z}} e^{\alpha nh/2} e^{-eh||r||^2}, \]
we have

**Theorem 4.** Given \( \alpha > 0 \) and \( 0 < \varepsilon \leq 1 \), for any step size \( h \) such that
\[ h \leq \frac{2\pi}{\log 3 + \alpha \log(\cos 1)^{-1}/2 + \log \varepsilon^{-1}}, \]
we have for \( ||r|| > 0 \)
\[ ||r||^{-\alpha} - S_\infty (||r||) \leq ||r||^{-\alpha}\varepsilon, \]
and
\[ S_\infty (||r||) < (\varepsilon + 1) ||r||^{-\alpha}, \]
where \( S_\infty \) is given in (4.6).

For a given accuracy \( \varepsilon \) and power \( \alpha \) (n.b., for the Coulomb potential \( \alpha = 1 \) and for the square \( \alpha = 2 \)), we may first select \( h \) and then, for a given range of values \( ||r|| \), truncate \( S_\infty (||r||) \) to yield a finite sum approximation in that range to obtain a finite sum \( S_F (||r||) \),
\[ S_F (||r||) = S_F (||r||; M_0, M_1, h) = \sum_{n=M_0}^{M_1} e^{\alpha nh/2} e^{-eh||r||^2}. \]
It is shown in [3] Theorem 5) that, for a fixed \( \alpha \), \( d < ||r|| < 1/d \) and any finite \( \varepsilon > 0 \), the step \( h = O (1/\log \varepsilon^{-1}) \) and the number of terms in (4.9) are estimated as \( M_1 - M_0 = O \left( \log d^{-1} \right) \) and \( M_1 - M_0 = O \left( (\log \varepsilon^{-1})^2 \right) \). By choosing \( d \) to be small (e.g. \( d = 10^{-15} \)) and selecting \( \varepsilon \) as needed, we replace the Coulomb potentials by their approximation for any user-selected accuracy and range. Importantly, the resulting approximating potential \( S_F (||r||) \) is in the Rollnik class so that the kernel (4.3) is that of a compact operator.

4.2. A compact operator for the Coulomb potential. As has already been mentioned, neither the Coulomb potential nor its square are in the Rollnik class. However, we show that for the Coulomb potential the operator with the kernel (4.4) is compact for functions in the Hilbert space \( \mathcal{H}_{\kappa,\delta} \) for any \( \delta > 0 \). Using (4.4) with the Coulomb potential,
\[ \sqrt{V} (p-p') = \frac{1}{||p-p'||}, \]
we consider the kernel...
Lemma 5. The operator with the kernel (4.10) is a Hilbert-Schmidt operator with the
Hilbert-Schmidt norm

\[ \| T \|_{HS} = \frac{1}{\kappa^2 \delta} \frac{\Gamma(1/2 + \delta)}{\Gamma(1 + \delta)} \frac{\pi^{3/2}}{\sqrt{\delta}}. \]

Proof. We prove Lemma 5 by explicitly evaluating the Hilbert-Schmidt norm by computing
the integral

\[ \| T \|_{HS}^2 = \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{1}{(\kappa^2 + \|p\|^2)^{1+\delta}} \frac{1}{\|p-p'\|^2} \frac{1}{(\kappa^2 + \|p'\|^2)^{1+\delta}} d^3p' d^3p. \]

We start with two integrals,

\[ \frac{1}{\|p\|^2} = \int_0^\infty e^{-\tau \|p\|^2} d\tau, \]

and

\[ \frac{1}{(\kappa^2 + \|p\|^2)^{1+\delta}} = \frac{1}{\Gamma(1 + \delta)} \int_0^\infty e^{-s(\kappa^2 + \|p\|^2)} s^\delta ds. \]

Substituting (4.12) and (4.13) into (4.11), we have

\[ \| T \|_{HS}^2 = \frac{1}{\Gamma(1 + \delta)^2} \int_0^\infty \int_0^\infty dsdt \tau \delta e^{-\tau(t + s)} \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} e^{-s\|p\|^2} e^{-t\|p'\|^2} e^{-\tau\|p-p'\|^2} d^3p' d^3p. \]

Evaluating the integral with the Gaussians, we obtain

\[ \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} e^{-s\|p\|^2} e^{-t\|p'\|^2} e^{-\tau\|p-p'\|^2} d^3p' d^3p = \frac{\pi^3}{(\tau (s+t)+ts)^{3/2}}. \]

Next we compute the integral over \( \tau \) and obtain

\[ \int_0^\infty \frac{\pi^3}{(\tau (s+t)+ts)^{3/2}} d\tau = \frac{2\pi^3}{(s+t)(st)^{1/2}}. \]

Finally, we compute

\[ \| T \|_{HS}^2 = \frac{2\pi^3}{\Gamma(1 + \delta)^2} \int_0^\infty e^{-\kappa^2(s+t)} \frac{1}{(s+t)(st)^{1/2-\delta}} dsdt = \frac{\pi^3 \Gamma(1/2 + \delta)^2}{\delta \Gamma(1 + \delta)^2} \frac{1}{\kappa^4 \delta}. \]

Remark 6. A product of two Coulomb potentials with distinct nuclear centers has the
same asymptotic decay in space as the square of the Coulomb potential considered above.
Therefore, the product in the momentum space will have the same dominant singularity at
the origin as the square of the Coulomb potential; other components of the potential are
sufficiently smooth in space so that their decay is faster in the momentum space and will
not cause the Hilbert-Schmidt norm to become unbounded.
5. BOUNDED OPERATORS

Next we consider two operators of interest and show that they are bounded.

5.1. Operator $G^{1/2}_{\mu}$. In the momentum space the operator $G^{1/2}_{\mu}$ is a multiplication operator by

$$\frac{1}{\mu^2 + \|p\|^2}$$

and, therefore, is a bounded operator with the norm $1/\mu$.

5.2. Matrix operator $\frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \mathcal{G}^{1/2}$. In momentum space we have

$$\frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \mathcal{G}^{1/2} = \left( \begin{array}{cccc} \frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & 0 & \frac{p_3}{\hbar c} & \frac{p_1 - ip_2}{\hbar c} \\ 0 & \frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & \frac{p_1 + ip_2}{\hbar c} & \frac{-p_3}{\hbar c} \\ \frac{p_1 + ip_2}{\hbar c} & \frac{-p_3}{\hbar c} & -\frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & 0 \\ 0 & 0 & 0 & -\frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} \end{array} \right)$$

and

$$\mathcal{G}^{1/2}(\boldsymbol{\kappa}, \boldsymbol{p}) = \mathcal{I} \frac{1}{(\boldsymbol{\kappa}^2 + \|\boldsymbol{p}\|^2)^{1/2}}.$$

We need to show that

$$\left\| \frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \mathcal{G}^{1/2} \varphi \right\|_2^2 \leq \text{Const} \|\varphi\|_2^2,$$

where the norm is the sum of squares of absolute values of the components and the integration in $\mathbb{R}^3$ is over the variable $\boldsymbol{p}$. For the proof we split the diagonal and off-diagonal parts of the matrix operator,

$$\frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \mathcal{G}^{1/2} = \mathcal{D} + \mathcal{O},$$

where

$$\mathcal{D} = (\boldsymbol{\kappa}^2 + \|\boldsymbol{p}\|^2)^{-1/2} \left( \begin{array}{cccc} \frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & 0 & 0 & 0 \\ 0 & \frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & 0 & 0 \\ 0 & 0 & -\frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & 0 \\ 0 & 0 & 0 & -\frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} \end{array} \right)$$

and

$$\mathcal{O} = (\boldsymbol{\kappa}^2 + \|\boldsymbol{p}\|^2)^{-1/2} \left( \begin{array}{cccc} 0 & 0 & \frac{p_3}{\hbar c} & \frac{p_1 - ip_2}{\hbar c} \\ 0 & 0 & \frac{p_1 + ip_2}{\hbar c} & \frac{-p_3}{\hbar c} \\ \frac{p_1 + ip_2}{\hbar c} & \frac{-p_3}{\hbar c} & 0 & 0 \\ \frac{p_3}{\hbar c} & \frac{p_1 - ip_2}{\hbar c} & 0 & 0 \end{array} \right).$$

Let $u(\boldsymbol{p}) = (u_1(\boldsymbol{p}), u_2(\boldsymbol{p}), u_3(\boldsymbol{p}), u_4(\boldsymbol{p}))^T$ and compute

$$\int_{\mathbb{R}^3} \left( \mathcal{O} u, \mathcal{O} u \right) d\boldsymbol{p} = \frac{1}{\hbar^2 c^2} \int_{\mathbb{R}^3} \frac{\|u(\boldsymbol{p})\|^2}{\boldsymbol{\kappa}^2 + \|\boldsymbol{p}\|^2} d\boldsymbol{p} \leq \frac{1}{\hbar^2 c^2} \int_{\mathbb{R}^3} \|u(\boldsymbol{p})\|^2 d\boldsymbol{p}$$

so that we have

$$\|\mathcal{O}\|_2 \leq \frac{1}{\hbar c}.$$
For the diagonal part, we have
\[
\int_{\mathbb{R}^3} \langle \mathcal{D} u, \mathcal{D} u \rangle \, dp = \frac{E}{\hbar^2 c^2} \int_{\mathbb{R}^3} \frac{1}{k^2 + ||p||^2} \|u(p)||^2 \, dp \\
+ \frac{m}{c^2} \int_{\mathbb{R}^3} \frac{1}{k^2 + ||p||^2} \left( |u_1(p)|^2 + |u_2(p)|^2 - |u_3(p)|^2 - |u_4(p)|^2 \right) \, dp
\]
or
\[
\int_{\mathbb{R}^3} \langle \mathcal{D} u, \mathcal{D} u \rangle \, dp \leq \left( \frac{E}{\hbar^2 c^2} + \frac{m}{c^2} \right) \int_{\mathbb{R}^3} \|u(p)||^2 \, dp
\]
so that
\[
\| \mathcal{D} \|_2 \leq \left( \frac{E}{\hbar^2 c^2} + \frac{m}{c^2} \right)^{1/2}
\]
and the operator in question is bounded.

6. Spectral structure of auxiliary family of integral operators

Since the product of a bounded and a compact operator is compact, we have shown that in the non-relativistic case the operator in (2.6),
\[
G_{\mu}^{1/2} V G_{\mu}^{1/2},
\]
is compact for any \( \mu > 0 \) and the operator \( \mathcal{A}(\kappa) \) in (2.19) is compact for any \( \kappa > 0 \).

The operator \( G_{\mu}^{1/2} V G_{\mu}^{1/2} \) is compact and self-adjoint, so we can apply the spectral theorem for compact self-adjoint operators in a Hilbert space. Therefore, we know that it has only discrete eigenvalues with the only possible accumulation point at zero, and its norm is equal to the largest absolute value of an eigenvalue. Considering

\[
\lambda_\mu \phi_\mu = -2 G_{\mu}^{1/2} V G_{\mu}^{1/2} \phi_\mu,
\]
we have
\[
\lambda_\mu \langle \phi_\mu, \phi_\mu \rangle = -2 \left< G_{\mu}^{1/2} V G_{\mu}^{1/2} \phi_\mu, \phi_\mu \right> = -2 \left< V G_{\mu}^{1/2} \phi_\mu, G_{\mu}^{1/2} \phi_\mu \right> = -2 \left< \psi_\mu, \psi_\mu \right>.
\]

Since the potential (2.2) is a negative definite multiplication operator (see Remark 7), it implies that \( \lambda_\mu > 0 \) for any \( \mu > 0 \). Note that from (2.1) we have
\[
\left< V(r) \psi_i, \psi_i \right> = E_i \left< \psi_i, \psi_i \right> - \frac{1}{2} \left< \nabla \psi_i, \nabla \psi_i \right>, \quad i = 1, \ldots, N,
\]
and, if energies \( E_i \) are negative, then on the solutions \( \psi_i \)
\[
\left< V(r) \psi_i, \psi_i \right> < 0.
\]
Each time we have \( \mu_i^2 = -E_i \), it implies that \( \lambda_\mu = 1 \) and \( \psi_{\mu_i} \) is a bound state satisfying (2.1). Also if \( \lambda_\mu = 1 \) then \( \mu_i^2 = -E_i \) so that we can seek unit eigenvalues of the auxiliary eigenvalue problem as a way of finding the bound states.

In the relativistic case, we consider the operator \( \mathcal{A}(\kappa) \),
\[
\mathcal{A}(\kappa) = -\frac{1}{\hbar^2 c^2} \left( \mathcal{H}_0 + E(\kappa) \right) \mathcal{A}_{\mathcal{C}}^{1/2}(\kappa) \mathcal{A}_{\mathcal{C}}^{1/2}(\kappa),
\]
which is a product of two self-adjoint operators. Since the potential (2.11) is a negative definite matrix multiplication operator (see Remark 2), the spectrum of \( \mathcal{A}(\kappa) \) is real. Indeed, let us define the operator
\[
\mathcal{B}(\kappa) = \mathcal{A}_{\mathcal{C}}^{1/2}(\kappa) (-\mathcal{A}_{\mathcal{C}}) \mathcal{A}_{\mathcal{C}}^{1/2}(\kappa),
\]
which is a compact positive-definite operator. Since the operator $\mathcal{B}(\kappa)$ is positive definite and self-adjoint, according to corollary of Lemma 7, $\mathcal{B}^{1/2}(\kappa)$ is well defined and is also a compact operator. Since $B$ is positive definite, $B^{-1/2}$ is well defined and is at least bounded. Since $\mathcal{A}(\kappa)$ is a compact operator, we can consider

$$\mathcal{B}^{1/2}(\kappa) \mathcal{A}(\kappa) B^{-1/2} = B^{1/2}(\kappa) \left[ \frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E(\kappa) P) \right] B^{1/2}(\kappa)$$

which is similar to $\mathcal{A}(\kappa)$ and is compact and self-adjoint. Therefore, we conclude that the spectrum of $\mathcal{A}(\kappa)$ is real and has only discrete eigenvalues with the only possible accumulation point at zero. Note that our considerations above are valid for any $\mu > 0$ and $\kappa > 0$. A slightly more general discussion of the spectra of the product of two self-adjoint operators can be found in Appendix 8.2.

7. CONVERGENCE OF ITERATION WITH AN ARBITRARY INITIALIZATION

We now turn to iterative solution of equations (2.18) and (2.6). We note that iterations used in practical computations when properly initialized do converge (see [10, 2]); however, we do not have a way to show that it will always be the case. Instead, we consider solving the auxiliary eigenvalue problems for a fixed parameter $\mu$ in (2.5) or $\kappa$ in (2.16). Since the operators are compact, the power iteration (combined with orthogonality between selected eigenfunctions), will always converge. In the non-linear Kohn-Sham and Hartree-Fock models, since components of the potential depend on the eigenfunctions, we assume that convergence is not affected by this nonlinear dependence and that solutions exists for all values of the parameter. Note that while this is an assumption, any theory that replaces the electron-electron interaction by an averaged field becomes unusable if the solution of the resulting nonlinear eigenvalue problem does not exist or cannot be obtained via an iteration. Once the solution is obtained for a particular value of the parameter, we can fix the potential and compute the derivative of the eigenvalue with respect to the parameter. This derivative can then be used to tune the parameter in order to arrive at $\lambda_\mu = 1$. We provide explicit expressions for the derivatives of the auxiliary eigenvalue with respect to the parameter in Appendices 8.3 and 8.4. These derivatives are derived assuming the potential is fixed.

As mentioned above, in practical computations we do not wait for the full convergence of the power iteration; splitting this iteration into two provides a way for understanding the reasons for convergence and a way to achieve convergence if, for some reason, the practical approach fails.

7.1. NUMERICAL DEMONSTRATION. The algorithm for computing bound states for relativistic equations of QC is described in [2]. In order to demonstrate the robust convergence regardless of starting condition, we consider an example of using relativistic equations for the hydrogen atom, which corresponds to a single atom with unit nuclear charge (i.e., $Z_\alpha = 1$ in equation 2.3). In all examples, the non-relativistic energy parameter for the Green’s function operator is fixed at $-0.5$ (this is the non-relativistic ground-state energy in the atomic units employed herein), with the corresponding relativistic energy obtained by adding $mc^2$. For ease of comparison, the relativistic energies reported in the text below are shifted by subtracting $mc^2$. Also, the number of iterations is fixed at 100 (we show only some of them). In QC, the Dirac 4-spinor is interpreted as comprising two 2-spinors — the “large” and “small” components, with the terminology arising because, for the sought positive-energy states that correspond to particles (in this case, electrons), the “large” component has significantly larger norm. For the free particle, the large and small components
of solutions to the Dirac equation are related through the so-called kinetic balance condition

\[ \psi_S = \frac{\hbar}{2ic} (\sigma_1 \frac{\partial}{\partial x_1} + \sigma_2 \frac{\partial}{\partial x_2} + \sigma_3 \frac{\partial}{\partial x_3}) \psi_L. \]

Using MADNESS with wavelet order 8 and a domain width of 100.0 atomic units, we examined four initial starting conditions as follows.

(1) The standard starting guess of the non-relativistic hydrogen atom solution in the first component of the large component with zero in the second and the small component being determined from the kinetic balance condition. The energies of the first two iterations are -0.500006490 and -0.500006270, with the second iteration being converged to all digits shown. Note that the exact Dirac-Coulomb energy for the hydrogen atom is -0.500006656..., but this is not obtained since we have fixed the energy parameter in the integral operator at the non-relativistic value.

(2) The initial large and small components from the previous starting guess are swapped, and the results shown in Figure 7.1. The non-relativistic ground state has zero-angular momentum (i.e., is an “s” function) and so, by construction, the small component initial guess constructed by the kinetic-balance condition has unit angular momentum (i.e., it is a “p” function). These symmetries are preserved in the relativistic solution. Hence, the initial guess constructed by swapping the large and small components of the expected non-relativistic initial guess in exact arithmetic is exactly orthogonal to the sought solution. This is apparent in the iteration as displayed in Figure 7.1 — the projection onto the exact solution starts at about machine precision (being literally numerical noise) and increases geometrically (circa 2x per iteration) until it reaches circa 0.3, whereupon it converges rapidly to one. The energy starts off large and negative (-1.9e4) but rapidly becomes positive and decays to close to zero (presumably dominated by a superposition of unbound electronic states). The energy stays near zero for many iterations until the projection upon the exact solution approaches 0.1, at which point the energy converges rapidly to the desired electronic ground state.

(3) The third test employed a random initial guess in which function values at the Gauss-Legendre quadrature points at 3 levels of refinement in each dimension were set to a random value sampled uniformly in [0,10] with the resulting function multiplied by a characteristic function to ensure it was zero on the edge of the computational volume to satisfy the free-space boundary conditions. Different random functions were used for each of the four components of the spinor. The energies of the first three iterations were -1.88e4, -0.04, -0.33, with convergence to nine significant figures of the energy being smoothly obtained in 17 iterations.

(4) The fourth test employed an initial guess that set one component of the large component to a spherical Gaussian with exponent 1e8 (i.e., a very high energy, unbound, electronic state) and the corresponding small component as determined by kinetic balance. The energies of the first 4 iterations were (3.1e4, 9.5e4, 3.2e2, and -0.40 respectively), and subsequently converged smoothly to nine significant figures of the energy c in 11 iterations overall.

We observe that independently of the initial guess, the iteration converges as expected. The only difference is, naturally, in the number of iterations needed to achieve convergence.
8. Appendix

8.1. Appendix A: Compact $A^*A$ implies $A$ is a compact operator.

Lemma 7. If $A^*A$ is a compact operator then $A$ is also a compact operator.

Proof. We have
\[
\|Ax\|^2 = \langle Ax, Ax \rangle = \langle A^*Ax, x \rangle \leq \|A^*Ax\| \|x\|
\]
and consider a bounded sequence $\{x_n\}$, $\|x_n\| \leq M$. Since $A^*A$ is a compact operator, there exist a convergent subsequence
\[
A^*Ax_{n_k}
\]
which is then a Cauchy sequence. This implies that $Ax_{n_k}$ is also a Cauchy sequence since, using the inequality above, we have
\[
\|Ax_{n_k} - Ax_{n_l}\|^2 = \|A(x_{n_k} - x_{n_l})\|^2 \leq 2M \|A^*Ax_{n_k} - A^*Ax_{n_l}\|.
\]
Therefore, the subsequence $Ax_{n_k}$ is convergent and $A$ is a compact operator. \qed

Corollary 8. If $A$ is a self-adjoint operator and $A^2$ is compact then $A$ is also a compact operator.
8.2. **Appendix B: Eigenvalues of the product of two self-adjoint operators.** We have

**Lemma 9.** Let $A$ be a self-adjoint operator and $B$ a positive (or a negative) definite self-adjoint operators. Then the spectrum of $AB$ is real.

Consider eigenvalue problem

$$ABx = \lambda x, \ x \neq 0.$$

**Proof.** We have

(8.1) \[ \langle BABx, x \rangle = \langle ABx, Bx \rangle = \lambda \langle x, Bx \rangle, \]

and observe that $\langle ABx, Bx \rangle$ is real since for any $y$, $\langle Ay, y \rangle = \langle y, Ay \rangle = \langle Ay, y \rangle$. Also for $x \neq 0$, $\langle x, Bx \rangle = (Bx, x) > 0$ since $B$ is a positive self-adjoint operator (less than zero if negative definite). We conclude that $\lambda$ is real. \(\square\)

**Remark 10.** Let $A$ and $B$ be self-adjoint and, as before, we arrive at (8.1). We have $\langle BABx, x \rangle$ is real and $\langle x, Bx \rangle$ is real. We conclude that $\lambda$ is real provided $\langle x, Bx \rangle \neq 0$. As a simple example consider

$$A = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad B = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}.$$

It is easy to check that the eigenvalues of $AB$ in this case are pure imaginary ($i$ and $-i$) and the eigenvectors of $AB$ are such that $\langle x, Bx \rangle = 0$. On the other hand, if

$$A = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \text{and} \quad B = \begin{pmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 & -1 \end{pmatrix},$$

then the eigenvalues of $A$ are $\{-1, 1, 1\}$, the eigenvalues of $B \{1, 1, -1\}$ so that neither $A$ or $B$ are positive/negative definite. However the eigenvalues of $AB$ are $\{-1, -1, 1\}$ and it is easy to check that the eigenvectors of $AB$ satisfy $\langle x, Bx \rangle \neq 0$.

**Lemma 11.** Let $A$ be a bounded and $B$ a compact positive (or a negative) definite self-adjoint operators. Then $AB$ has only discrete real eigenvalues with the the only possible accumulation point at zero.

**Proof.** Let us consider $B^{1/2}AB^{1/2}$. Since $B$ is positive definite, $B^{1/2}$ exist and is self-adjoint. According to Corollary 8, $B^{1/2}$ is a compact operator and, therefore, $B^{1/2}AB^{1/2}$ is also compact. Since it is self-adjoint, the spectral theorem for compact operators in a Hilbert space is applicable and we know that its spectrum is discrete, with the only possible accumulation point at zero. Since $AB = B^{-1/2} (B^{1/2}AB^{1/2}) B^{1/2}$, it has the same spectrum as $B^{1/2}AB^{1/2}$. \(\square\)

8.3. **Appendix C: Monotone dependence of eigenvalue on the parameter in non-relativistic case.** Let us consider

(8.2) \[ \lambda_{\mu} \psi_{\mu} = -G_{\mu} V \psi_{\mu}, \ \lambda_{\mu} > 0, \]

or

(8.3) \[ \lambda_{\mu} \phi_{\mu} = -G^{1/2}_{\mu} V G^{1/2}_{\mu} \phi_{\mu}, \ |\phi_{\mu}| = 1, \ \lambda_{\mu} > 0, \]
where $G_{\mu}$ is the Green’s function

$$G_{\mu}(p) = \frac{1}{\mu^2 + ||p||^2},$$

in the momentum space and $\phi_{\mu} = G_{\mu}^{-1/2}\psi_{\mu}$. Here we assume that the potential $V$ does not depend on $\mu$. Since within the iteration potential does depend on $\mu$, our conclusion is applicable once the iteration converged so that the potential can be fixed.

We use

$$\frac{dG_{\mu}}{d\mu} = -2\mu G_{\mu}^2$$

in our derivations below.

**Lemma 12.** If the potential $V$ does not depend on the parameter $\mu$, then the derivative of an eigenvalue with respect to the parameter $\mu$ is negative,

$$\frac{d\lambda_{\mu}}{d\mu} = -2\mu \lambda_{\mu} \left\| G_{\mu}^{1/2} \phi_{\mu} \right\|.$$  (8.4)

**Proof.** Differentiating (8.2), we have

$$\frac{d\lambda_{\mu}}{d\mu} \psi_{\mu} + \lambda_{\mu} \frac{d\psi_{\mu}}{d\mu} = 2\mu G_{\mu}^2 V \psi_{\mu} - G_{\mu} V \frac{d\psi_{\mu}}{d\mu},$$

and computing the inner product with $G_{\mu}^{-1} \psi_{\mu}$, obtain

$$\frac{d\lambda_{\mu}}{d\mu} \left\langle \psi_{\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle + \lambda_{\mu} \left\langle \frac{d\psi_{\mu}}{d\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle = 2\mu \left\langle G_{\mu}^2 V \psi_{\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle - \left\langle G_{\mu} V \frac{d\psi_{\mu}}{d\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle.$$

Since

$$\lambda_{\mu} G_{\mu}^{-1} \psi_{\mu} = -V \psi_{\mu}$$

and $G_{\mu}$ and $V$ are symmetric operators, we have

$$\frac{d\lambda_{\mu}}{d\mu} \left\langle \psi_{\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle = 2\mu \left\langle G_{\mu}^2 V \psi_{\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle$$

or, using (8.2),

$$\frac{d\lambda_{\mu}}{d\mu} \left\langle \psi_{\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle = -2\mu \lambda_{\mu} \left\langle G_{\mu} \psi_{\mu}, G_{\mu}^{-1} \psi_{\mu} \right\rangle = -2\mu \lambda_{\mu} \left\| \psi_{\mu} \right\|^2$$

yielding (8.4). \qed

**8.4. Appendix D: Dependence of eigenvalue on the parameter in the relativistic case.**

Next we consider the auxiliary eigenvalue problem for the Dirac equation

$$\lambda(\kappa) \psi(\kappa) = -\frac{1}{\hbar^2 c^2} (H_0 + E(\kappa) \mathcal{F}(\kappa)) \psi(\kappa),$$  (8.5)

where $E < mc^2$

$$E = \left( m^2 c^4 - \kappa^2 c^2 \hbar^2 \right)^{1/2},$$

and

$$\frac{dE}{d\kappa} = -\kappa c^2 \hbar^2 \left( m^2 c^4 - \kappa^2 c^2 \hbar^2 \right)^{-1/2} = -\frac{c^2 \hbar^2}{E}.$$  

In (8.5)

$$\mathcal{F}(\kappa) = G(\kappa) \mathcal{J},$$
Applying \( G \) to both sides of (8.6), we have

\[
\frac{d}{d \kappa} (\mathcal{H}_0 + E \mathcal{I}) = \left( \begin{array}{ccc}
\frac{\sigma_0 mc^2}{\hbar^2} & 0 & \frac{\sigma_1 \frac{d}{d \sigma_1} + \sigma_2 \frac{d}{d \sigma_2} + \sigma_3 \frac{d}{d \sigma_3}}{\hbar^2} \\
\frac{\sigma_0 mc^2}{\hbar^2} & 0 & \frac{-\sigma_0 mc^2}{\hbar^2} \\
\frac{\sigma_0 mc^2}{\hbar^2} & 0 & \frac{-\sigma_0 mc^2}{\hbar^2}
\end{array} \right).
\]

Lemma 13. If the potential \( V \) does not depend on the parameter \( \mu \), then for the derivative of an eigenvalue in (8.5), we have

\[
\frac{d}{d \kappa} = \kappa \lambda (\kappa) \frac{1}{\hbar^2 c^2} \left( \psi, (\mathcal{H}_0 + E \mathcal{I})^{-1} \psi \right) \left( - \frac{1}{E (\kappa)} \left\| G^{1/2} \mathcal{H}_0 \psi \right\|^2 + E (\kappa) \left\| G^{1/2} \psi \right\|^2 \right).
\]

In the momentum space

\[
\frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) = \left( \begin{array}{ccc}
\frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & 0 & \frac{p_1}{\hbar^2} \\
0 & \frac{m}{\hbar^2} + \frac{E}{\hbar^2 c^2} & \frac{-p_3}{\hbar^2} \\
\frac{p_3}{\hbar^2} & \frac{-p_3}{\hbar^2} & \frac{-p_3}{\hbar^2}
\end{array} \right)
\]

and this operator commutes with \( \mathcal{I} (\kappa) \).

As in the non-relativistic case, the expression for the derivative does not have explicit dependence on the potential. However, in this case the derivative may not be sign definite. In both, non-relativistic and relativistic cases, expressions for the derivative can be used to set up a combination of the power iteration and the Newton method to solve for \( \lambda (\kappa) = 1 \) in order to compute the bound states

**Proof.** We have

(8.6)

\[
\frac{d}{d \kappa} \lambda (\kappa) \psi + \lambda (\kappa) \frac{d}{d \kappa} \psi = -\frac{1}{\hbar^2 c^2} \left( \mathcal{H}_0 + E \mathcal{I} \right) \frac{d}{d \kappa} \mathcal{I} \psi - \frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \frac{d}{d \kappa} \mathcal{I} \psi - \frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \frac{d}{d \kappa} \mathcal{I} \psi
\]

and evaluate the inner product of both sides of (8.6) with \( \mathcal{I}^{-1} (\mathcal{H}_0 + E \mathcal{I})^{-1} \psi \). We first show that

\[
\left\langle \lambda (\kappa) \frac{d}{d \kappa} \mathcal{I}^{-1} (\mathcal{H}_0 + E \mathcal{I})^{-1} \psi \right\rangle = -\left\langle \frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \mathcal{I} \frac{d}{d \kappa} \mathcal{I} \psi \right\rangle.
\]

Applying \( \mathcal{I}^{-1} (\mathcal{H}_0 + E \mathcal{I})^{-1} \) on both sides of (8.5), we have

\[
\lambda (\kappa) \mathcal{I}^{-1} (\kappa) (\mathcal{H}_0 + E (\kappa) \mathcal{I})^{-1} \psi (\kappa) = -\frac{1}{\hbar^2 c^2} \mathcal{I} \psi (\kappa)
\]

so that

\[
\left\langle \lambda (\kappa) \frac{d}{d \kappa} \mathcal{I}^{-1} (\mathcal{H}_0 + E \mathcal{I})^{-1} \psi \right\rangle = -\frac{1}{\hbar^2 c^2} \left\langle \frac{d}{d \kappa} \mathcal{I} \psi, \mathcal{I} \psi \right\rangle.
\]

Since \( \mathcal{H}_0 + E \mathcal{I} \) and \( \mathcal{I} \) commute, we also have

\[
-\left\langle \frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{I}) \mathcal{I} \frac{d}{d \kappa} \mathcal{I}^{-1} (\mathcal{H}_0 + E \mathcal{I})^{-1} \psi \right\rangle = -\frac{1}{\hbar^2 c^2} \left\langle \frac{d}{d \kappa} \mathcal{I} \psi, \mathcal{I} \psi \right\rangle.
\]
We thus obtain
\[
\frac{d \lambda (\kappa)}{d \kappa} \left\langle \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle = - \frac{1}{\hbar^2 c^2} \frac{dE}{d\kappa} \left\langle \mathcal{G} \mathcal{V} \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle + \\
\frac{2\kappa}{\hbar^2 c^2} \left\langle (\mathcal{H}_0 + E \mathcal{J}) \mathcal{G}^2 \mathcal{V} \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle,
\]
(8.7)

Using
\[
- \frac{1}{\hbar^2 c^2} \mathcal{G} \mathcal{V} \psi = - \frac{1}{\hbar^2 c^2} (\mathcal{H}_0 + E \mathcal{J})^{-1} (\mathcal{H}_0 + E \mathcal{J}) \mathcal{G} \mathcal{V} \psi = (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi,
\]
and
\[
(\mathcal{H}_0 + E \mathcal{J})^{-1} = \frac{1}{\hbar^2 c^2} \mathcal{G} (\mathcal{H}_0 - E \mathcal{J}),
\]
we have for the first term on the right hand side of (8.7)
\[
- \frac{1}{\hbar^2 c^2} \frac{dE}{d\kappa} \left\langle \mathcal{G} \mathcal{V} \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle = - \kappa \lambda (\kappa) \frac{\hbar^2}{E} \left\langle \mathcal{G} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle
\]
\[
= - \kappa \lambda (\kappa) \frac{1}{E} \frac{1}{\hbar^2 c^2} \left\langle \mathcal{G} (\mathcal{H}_0 - E \mathcal{J}) \psi, (\mathcal{H}_0 - E \mathcal{J}) \psi \right\rangle
\]
\[
= - \kappa \lambda (\kappa) \frac{1}{E} \frac{1}{\hbar^2 c^2} \left\langle (\mathcal{G} \mathcal{H}_0 \psi, \mathcal{H}_0 \psi) - 2E (\mathcal{G} \mathcal{H}_0 \psi, \psi) + E^2 (\mathcal{G} \psi, \psi) \right\rangle
\]
\[
= - \kappa \lambda (\kappa) \frac{1}{E} \frac{1}{\hbar^2 c^2} \left( \| \mathcal{G}^{1/2} \mathcal{H}_0 \psi \|^2 - 2E (\mathcal{G} \mathcal{H}_0 \psi, \psi) + E^2 \| \mathcal{G}^{1/2} \psi \|^2 \right),
\]
and, for the second,
\[
\frac{2\kappa}{\hbar^2 c^2} \left\langle (\mathcal{H}_0 + E \mathcal{J}) \mathcal{G}^2 \mathcal{V} \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle = - 2\kappa \lambda (\kappa) \left\langle \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle
\]
\[
= - 2\kappa \lambda (\kappa) \left\langle \psi, (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle
\]
\[
= - 2\kappa \lambda (\kappa) \left( \psi, (\mathcal{H}_0 - E \mathcal{J}) \psi \right)
\]
\[
= - 2\kappa \lambda (\kappa) \frac{1}{\hbar^2 c^2} \left( \psi, (\mathcal{H}_0 - E \mathcal{J}) \psi \right)
\]
\[
= - 2\kappa \lambda (\kappa) \frac{1}{\hbar^2 c^2} \left( \psi, (\mathcal{H}_0 - E \mathcal{J}) \psi \right)
\]
\[
= - 2\kappa \lambda (\kappa) \frac{1}{\hbar^2 c^2} \left( \psi, (\mathcal{H}_0 - E \mathcal{J}) \psi \right)
\]
Also using
\[
\left\langle \psi, \mathcal{G}^{-1} (\mathcal{H}_0 + E \mathcal{J})^{-1} \psi \right\rangle = \frac{1}{\hbar^2 c^2} \left( \psi, (\mathcal{H}_0 - E \mathcal{J}) \psi \right),
\]
we obtain from (8.7)
\[
\frac{d \lambda (\kappa)}{d \kappa} (\psi, (\mathcal{H}_0 - E \mathcal{J}) \psi) = \kappa \lambda (\kappa) \frac{1}{\hbar^2 c^2} \left( - \frac{1}{E(\kappa)} \left\| \mathcal{G}^{1/2} \mathcal{H}_0 \psi \right\|^2 + E(\kappa) \left\| \mathcal{G}^{1/2} \psi \right\|^2 \right).
\]
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