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On the physical meaning of the ZORA Hamiltonian†

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By expanding the Foldy–Wouthuysen representation of the Dirac equation near the free-particle solution it is shown that the Hamiltonian of the zeroth-order regular approximation (ZORA) leads to an infinite summation of the leading relativistic corrections to the free-particle, non-relativistic energy. The analysis of the perturbation expansion of the ZORA Hamiltonian reveals that the ZORA Hamiltonian recovers all terms of the Breit–Pauli theory to second order. This result is general and applies not only to hydrogen-like atomic ions (as was demonstrated before) but also to a wide variety of physical problems. ZORA is analogous to the random phase approximation in many-body theory in the sense that both methods include an infinite-order summation of the asymptotically non-vanishing terms. This highlights the difference between ZORA and the Douglas–Kroll method, with the latter being analogous to finite-order many-body perturbation theory. On the basis of this analysis the performance of ZORA when calculating various molecular properties is discussed.

1. Introduction

The zeroth-order regular approximation (ZORA) [1–4] to the full relativistic Hamiltonian [5] is currently a widely used approach in relativistic quantum chemistry [6]. The concept of the regular approximation is based on an expansion of the full four-component relativistic Hamiltonian with respect to a potential-dependent perturbation parameter [3, 4]. Already at the zeroth order this expansion contains relativistic corrections to the non-relativistic energy. At variance with the standard Breit–Pauli approach [7], the ZORA Hamiltonian is bounded from below [8] and can be used in quasi-variational calculations. In actual atomic and molecular calculations, the ZORA method (and related methods [9–11]) provides an excellent description of valence and sub-valence electrons in heavy elements [3, 4, 6, 8].

However, little is known about the reasons of such an outstanding performance of ZORA (and related methods) in atomic and molecular calculations. The now-standard way of deriving the regularly approximated relativistic Hamiltonians is the expansion [3, 4, 8, 9, 12] of the full four-component relativistic Hamiltonian with respect to the parameter $E/(2mc^2 - V)$, which is small for a singular potential V such as the Coulomb potential. While for the expansion this guarantees a good convergence property, quite little is revealed about the zeroth-order approximation itself.

The relationship between ZORA and other quasi-variational approximate relativistic theories such as the Douglas–Kroll method [13–15] also remains unclear. In the latter approach, the exact Foldy–Wouthuysen transformation [16] is factorized into a product of two terms, a free-particle transformation which is known in closed algebraic form and a field-dependent part which is not known in a closed form but is expanded up to a certain order in terms of the potential field [13–15, 17]. Although the Douglas–Kroll method has been criticized in the literature from a purely theoretical point of view [17], it has proven successful in actual atomic and molecular calculations [18]. The use of a perturbation expansion in the derivation of the Douglas–Kroll method provides a solid foundation for the method and enables one to make a judgement on the method's applicability to various problems in quantum physics.

The perturbational treatment was also applied to the derivation of ZORA [19, 20], whereby it has been shown that the ZORA Hamiltonian is the lowest-order approximation to an alternative (two-parametric) direct perturbational expansion of the Dirac equation. While it is commonly believed that the ZORA Hamiltonian contains partial infinite summations of terms of increasingly high order in $1/c^2$ [17], the nature of these higher-order terms remains unsolved. For one example of hydrogen-like atomic ions, it was demonstrated numerically [20] that the ZORA Hamiltonian recovers all terms of the Breit–Pauli Hamiltonian. However, it still remains unclear whether this feature of ZORA holds only for hydrogen-like ions or for other physical problems (such as the harmonic oscillator, etc.) too.

†Dedicated to Professor Petr Čársky on the occasion of his 60th birthday

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The primary goal of the present work is to analyse the physical nature of the terms contained in the zeroth-order regular Hamiltonian and to connect ZORA to other approximate approaches in relativistic quantum theory. In doing so, we proceed with the study of the exact relativistic Hamiltonian for electronic states near the free-particle solution and consider the expansion of the exact electronic Hamiltonian with respect to the potential field. The use of such an expansion for the analysis of ZORA is inspired by the asymptotic behaviour of the ZORA Hamiltonian which converts to the free-particle non-relativistic Hamiltonian for vanishing potential [12]. In section 2 the derivation of the regular approximation is briefly surveyed, the expansion of the relativistic electronic Hamiltonian near the free-particle solution is presented and the ZORA Hamiltonian is traced back to its origin.

2. Analysis of the ZORA Hamiltonian

2.1. *The standard derivation of the ZORA Hamiltonian*

The first step in deriving the regular approximation is decoupling of the electronic and positronic solutions of the Dirac equation by means of a unitary transformation known as a Foldy–Wouthuysen (FW) transformation [16]. The application of the FW transformation to the Dirac Hamiltonian is described in many publications (see, e.g. [9, 17, 21]) and textbooks (see, e.g. [7]) and is not repeated here for reasons of brevity. The resulting equation can be cast into the form of equation (1) [9],

$$\hat{H}^{\mathrm{FW}}\Psi_{\mathrm{L}} = E\left(1+\hat{X}^{\dagger}\hat{X}\right)\Psi_{\mathrm{L}}\,, \tag{1}$$

where Ψ_{L} is the large component of the Dirac wavefunction

$$\Psi_{\mathrm{D}} = \begin{pmatrix}\Psi_{\mathrm{L}}\\ \Psi_{\mathrm{S}}\end{pmatrix},$$

the Hamiltonian is given in equation (2) [9, 21]

$$\hat{H}^{\mathrm{FW}} = V + c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X} + \hat{X}^{\dagger}c(\boldsymbol{\sigma}\cdot\mathbf{p}) + \hat{X}^{\dagger}\left(V-2mc^2\right)\hat{X} \tag{2}$$

and $\hat{X}$ is the operator which connects the large and small components of Ψ_{D} via equation (3) [9, 21]

$$\Psi_{\mathrm{S}} = \hat{X}\Psi_{\mathrm{L}}. \tag{3}$$

The operator $\hat{X}$ satisfies condition (4) [9, 21].

$$c(\boldsymbol{\sigma}\cdot\mathbf{p}) = 2mc^2\hat{X} + \left[\hat{X}, V\right] + \hat{X}c(\boldsymbol{\sigma}\cdot\mathbf{p})\hat{X}. \tag{4}$$

In equations (2) and (4), $\boldsymbol{\sigma}$ is the vector of the Pauli matrices $\boldsymbol{\sigma} = (\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y, \boldsymbol{\sigma}_z)$ [22], $\mathbf{p} = -\mathrm{i}\hbar\nabla$ is the momentum operator, m is the rest mass of the electron and c is the velocity of light.

Assuming that the exact solution to the Dirac equation is known, the operator $\hat{X}$ can be represented as in equation (5) [9],

$$\hat{X} = \frac{c}{2mc^2 - V + E}(\boldsymbol{\sigma}\cdot\mathbf{p}), \tag{5}$$

and equation (1) can be re-written in the form of equation (6),

$$\left(V + (\boldsymbol{\sigma}\cdot\mathbf{p})\left[\frac{c^2}{2mc^2-V+E} + \frac{c^2E}{(2mc^2-V+E)^2}\right](\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}} = E\left(1 + (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(2mc^2-V+E)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}\,, \tag{6}$$

where E is the Dirac eigen energy corresponding to the known solution.

Expanding equation (6) with respect to the parameter $E/(2mc^2 - V)$ leads [9] in the zeroth order to the ZORA Hamiltonian in equation (7).

$$\hat{H}^{\mathrm{ZORA}} = V + \frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{1}{1+(V/2mc^2)}(\boldsymbol{\sigma}\cdot\mathbf{p}). \tag{7}$$

2.2. *Expansion of equation (1) near the free-particle solution*

Let us assume that the potential V in equations (1) and (6) is weak ($-2mc^2 \ll V \ll 2mc^2$) and can be considered as a perturbation. Multiplying V in equation (6) by a perturbation parameter λ, expanding the wavefunction Ψ_{L}, the energy E, the Hamiltonian $\hat{H}^{\mathrm{FW}}$ and the wavefunction metric $1 + \hat{X}^{\dagger}\hat{X}$ in powers of the parameter λ as in equations (8)–(11),

$$\Psi_{\mathrm{L}} = \Psi_{\mathrm{L}}^{(0)} + \lambda\Psi_{\mathrm{L}}^{(1)} + \lambda^2\Psi_{\mathrm{L}}^{(2)} + \ldots, \tag{8}$$

$$E = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \ldots, \tag{9}$$

$$\begin{aligned}\hat{H}^{\mathrm{FW}} &= \lambda V + (\boldsymbol{\sigma}\cdot\mathbf{p})\left[\frac{c^2}{2mc^2 - \lambda V + E} + \frac{c^2E}{(2mc^2-\lambda V+E)^2}\right](\boldsymbol{\sigma}\cdot\mathbf{p})\\ &= (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(0)}+mc^2)}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\\ &\quad + \lambda\left(V + (\boldsymbol{\sigma}\cdot\mathbf{p})\right.\\ &\quad \left.\times\frac{c^2((E^{(0)}+2mc^2)V - 2E^{(0)}(E^{(1)}-V))}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\\ &\quad + \lambda^2(\boldsymbol{\sigma}\cdot\mathbf{p})\\ &\quad \times\left[\frac{2c^2(E^{(0)}(E^{(1)}-V)(E^{(1)}-2V) - mc^2(E^{(1)2}-V^2))}{(E^{(0)}+2mc^2)^4}\right.\\ &\quad \left.-\frac{2c^2E^{(0)}E^{(2)}}{(E^{(0)}+2mc^2)^3}\right](\boldsymbol{\sigma}\cdot\mathbf{p}) + \ldots,\end{aligned} \tag{10}$$

$$
\begin{aligned}
1+\hat{X}^{\dagger}\hat{X} &= 1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(2mc^2-\lambda V+E)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}) \\
&= 1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}) \\
&\quad -\lambda(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(1)}-V)}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p}) \\
&\quad +\lambda^2(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2(3(E^{(1)}-V)^2-2E^{(2)}(E^{(0)}+2mc^2))}{(E^{(0)}+2mc^2)^4} \\
&\quad \times(\boldsymbol{\sigma}\cdot\mathbf{p})+\ldots
\end{aligned}
\tag{11}
$$

and collecting the terms of the same order in λ, the following equations can be obtained. In the zeroth order, one has equation (12), which is the free-particle Dirac equation upon applying the free-particle FW transformation.

$$
\begin{aligned}
&(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(0)}+mc^2)}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(0)} \\
&\quad = E^{(0)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(0)}.
\end{aligned}
\tag{12}
$$

In first order, equation (13) emerges.

$$
\begin{aligned}
&(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(0)}+mc^2)}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(1)} \\
&\quad +\left(V+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2((E^{(0)}+2mc^2)V-2E^{(0)}(E^{(1)}-V))}{(E^{(0)}+2mc^2)^3}\right. \\
&\qquad \left.\times(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(0)} \\
&= E^{(1)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(0)} \\
&\quad -E^{(0)}(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(1)}-V)}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(0)} \\
&\quad +E^{(0)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(1)}.
\end{aligned}
\tag{13}
$$

In second order of λ, one obtains equation (14).

$$
\begin{aligned}
&(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(0)}+mc^2)}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(2)} \\
&\quad +\left(V+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2((E^{(0)}+2mc^2)V-2E^{(0)}(E^{(1)}-V))}{(E^{(0)}+2mc^2)^3}\right. \\
&\qquad \left.\times(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(1)}+(\boldsymbol{\sigma}\cdot\mathbf{p}) \\
&\qquad \times\left[\frac{2c^2(E^{(0)}(E^{(1)}-V)(E^{(1)}-2V)-mc^2(E^{(1)^2}-V^2))}{(E^{(0)}+2mc^2)^4}\right. \\
&\qquad \left.-\frac{2c^2E^{(0)}E^{(2)}}{(E^{(0)}+2mc^2)^3}\right](\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(0)} \\
&= E^{(0)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(2)} \\
&\quad +E^{(1)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(1)} \\
&\quad +E^{(2)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}}^{(0)} \\
&\quad -E^{(0)}(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(1)}-V)}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(1)} \\
&\quad -E^{(1)}(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(1)}-V)}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(0)} \\
&\quad +E^{(0)}(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2(3(E^{(1)}-V)^2-2E^{(2)}(E^{(0)}+2mc^2))}{(E^{(0)}+2mc^2)^4} \\
&\quad \times(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_{\mathrm{L}}^{(0)}.
\end{aligned}
\tag{14}
$$

Assuming that $E^{(0)} \ll mc^2$, $E^{(1)} \ll mc^2$ and $E^{(2)} \ll mc^2$ and taking the non-relativistic limit of equations (12)–(14), one can derive equations (15)–(17),

$$
\left(\hat{T}-E^{(0)}\right)\Psi_{\mathrm{L}}^{(0)}=0\,, \tag{15}
$$

$$
\left(\hat{T}-E^{(0)}\right)\Psi_{\mathrm{L}}^{(1)}=\left(E^{(1)}-V-\frac{1}{4m^2c^2}\hat{W}_0\right)\Psi_{\mathrm{L}}^{(0)}, \tag{16}
$$

$$
\begin{aligned}
\left(\hat{T}-E^{(0)}\right)\Psi_{\mathrm{L}}^{(2)} &= \left(E^{(1)}-V-\frac{1}{4m^2c^2}\hat{W}_0\right)\Psi_{\mathrm{L}}^{(1)} \\
&\quad +\left(E^{(2)}-\frac{1}{8m^3c^4}\hat{W}_1\right)\Psi_{\mathrm{L}}^{(0)},
\end{aligned}
\tag{17}
$$

$$
\vdots
$$

where $\hat{T}=(\boldsymbol{\sigma}\cdot\mathbf{p})^2/(2m)$ is the non-relativistic kinetic energy operator and $\hat{W}_k$ is given in equation (18)

$$
\hat{W}_k=(\boldsymbol{\sigma}\cdot\mathbf{p})V^{k+1}(\boldsymbol{\sigma}\cdot\mathbf{p}). \tag{18}
$$

Equation (15) is obviously the non-relativistic free-particle Schrödinger equation and equation (16) yields the lowest-order relativistic and potential energy correction to it, etc.

Taking summation of equations (15)–(17) and regrouping terms, equation (19) can be derived.

$$
\begin{aligned}
&\left(\hat{T}+V+\left(\frac{1}{4m^2c^2}\hat{W}_0+\frac{1}{8m^3c^4}\hat{W}_1+\ldots\right)\right) \\
&\quad \times(\Psi_{\mathrm{L}}^{(0)}+\Psi_{\mathrm{L}}^{(1)}+\Psi_{\mathrm{L}}^{(2)}+\ldots) \\
&= \left(V+\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})\left(1+\frac{V}{2mc^2}+\left(\frac{V}{2mc^2}\right)^2+\ldots\right)(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}} \\
&= \left(V+\frac{1}{2m}(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{1}{1-\frac{V}{2mc^2}}(\boldsymbol{\sigma}\cdot\mathbf{p})\right)\Psi_{\mathrm{L}} \\
&= (E^{(0)}+E^{(1)}+E^{(2)}+\ldots)(\Psi_{\mathrm{L}}^{(0)}+\Psi_{\mathrm{L}}^{(1)}+\Psi_{\mathrm{L}}^{(2)}+\ldots)=E\Psi_{\mathrm{L}}.
\end{aligned}
\tag{19}
$$

The third line of equation (19) is obviously the ZORA Hamiltonian. Note that all summations in equation (19) stretch up to infinite order. Thus, the ZORA Hamiltonian includes the leading relativistic corrections to the free-particle non-relativistic Hamiltonian up to an infinite order.

With the help of equations (15)–(17), the expectation values of the operators $c^2\hat{W}_k/(2mc^2)^{k+2}$ can be identified as the perturbative relativistic corrections of the $(k+1)$th order to the non-relativistic energy. Indeed, multiplying equations (15)–(17) with $\Psi_{\mathrm{L}}^{(0)\dagger}$ from the left, integrating and using the hermiticity property of $\hat{T}$ and $\hat{W}_k$ one obtains in the non-relativistic limit equations (20) and (21)

$$E^{(1)} = \left\langle \Psi_{\mathrm{L}}^{(0)} | V | \Psi_{\mathrm{L}}^{(0)} \right\rangle + \left\langle \Psi_{\mathrm{L}}^{(0)} \left| \frac{\hat{W}_0}{4m^2c^2} \right| \Psi_{\mathrm{L}}^{(0)} \right\rangle, \quad (20)$$

$$E^{(2)} = \left\langle \Psi_{\mathrm{L}}^{(0)} \left| \frac{\hat{W}_1}{8m^3c^4} \right| \Psi_{\mathrm{L}}^{(0)} \right\rangle, \quad (21)$$

$$\vdots$$

For complete expressions of the first- and second-order corrections see Appendix A.

The use of infinite summations in equation (19) makes the interpretation proposed applicable not only to situations where the potential is weak but also to bound states in a strong potential field. In such a case, the wavefunction expansion with respect to the potential field cannot be truncated at finite order [17]. However, infinite summations with regard to both the wavefunction expansion and the Hamiltonian expansion leads to theoretically consistent descriptions.

2.3. *Evaluation of* $\langle \hat{W}_k \rangle$

Let us consider the expectation values $\langle \Psi | \hat{W}_k | \Psi \rangle = \langle \Psi | (\boldsymbol{\sigma}\cdot\mathbf{p}) V^{k+1} (\boldsymbol{\sigma}\cdot\mathbf{p}) | \Psi \rangle$ where Ψ is an arbitrary wavefunction. The wavefunction Ψ can be decomposed in terms of the eigenfunctions Ψ_k of the free-particle Schrödinger equation. Note that Ψ_k are identical to $\Psi_{\mathrm{L}}^{(0)}$ from the previous subsection. For the purpose of normalizing Ψ_k, it is assumed that the particle is constrained to move in a box of large but finite volume.

Functions Ψ_k form a complete set of functions, i.e. any arbitrary function defined on the same set of variables can be expanded in terms of these functions. Because the free-particle Hamiltonian commutes with the linear momentum operator, the functions $(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_k$ are simultaneously eigenfunctions of the free-particle Hamiltonian and form a complete set of functions too. Consequently, a function $V(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi$ can be decomposed as in equation (22)

$$V(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi = \sum_k c_k (\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_k. \quad (22)$$

Multiplying equation (22) by $(\boldsymbol{\sigma}\cdot\mathbf{p})\Psi_k^\dagger$ from the left and integrating one finds the coefficients c_k,

$$c_k = (2mE_k)^{-1} \langle \Psi_k | (\boldsymbol{\sigma}\cdot\mathbf{p}) V (\boldsymbol{\sigma}\cdot\mathbf{p}) | \Psi \rangle, \quad (23)$$

where E_k are the corresponding eigen energies of the non-relativistic free-particle Hamiltonian. Let us use equations (22) and (23) in the evaluation of the expectation value of operator $\hat{W}_1$ according to equation (24)

$$\begin{aligned} \frac{1}{8m^3c^4}\langle \Psi | \hat{W}_1 | \Psi \rangle &= \frac{1}{8m^3c^4}\langle \Psi | (\boldsymbol{\sigma}\cdot\mathbf{p}) V V (\boldsymbol{\sigma}\cdot\mathbf{p}) | \Psi \rangle \\ &= \frac{1}{8m^3c^4}\sum_k \frac{\langle \Psi | (\boldsymbol{\sigma}\cdot\mathbf{p}) V (\boldsymbol{\sigma}\cdot\mathbf{p}) | \Psi_k \rangle \langle \Psi_k | (\boldsymbol{\sigma}\cdot\mathbf{p}) V (\boldsymbol{\sigma}\cdot\mathbf{p}) | \Psi \rangle}{2mE_k} \\ &= \sum_k \left\langle \Psi \left| \frac{(\boldsymbol{\sigma}\cdot\mathbf{p}) V (\boldsymbol{\sigma}\cdot\mathbf{p})}{4m^2c^2} \right| \Psi_k \right\rangle \frac{1}{E_k} \left\langle \Psi_k \left| \frac{(\boldsymbol{\sigma}\cdot\mathbf{p}) V (\boldsymbol{\sigma}\cdot\mathbf{p})}{4m^2c^2} \right| \Psi \right\rangle. \end{aligned} \quad (24)$$

Expressions for the higher-order terms such as $[16m^4c^6]^{-1}\langle \Psi_i | \hat{W}_2 | \Psi_i \rangle$, etc., can be derived in a similar way. Equation (24) can formally be cast into the canonical second-order expression in the Rayleigh–Schrödinger perturbation theory by adding a trivial solution to the set of eigenfunctions of the free-particle Hamiltonian. Then, the denominator in equation (24) can formally be written as $E_k - E_0$, where E_0 is zero. Although such a procedure is purely formal, it helps to recognize the expectation value of the ZORA Hamiltonian as the result of a summation of the perturbation series up to infinite order. The term $[4m^2c^2]^{-1}\langle \Psi | \hat{W}_0 | \Psi \rangle$ then plays the role of the first-order perturbation correction.

Before starting the analysis of the lowest-order relativistic correction $[4m^2c^2]^{-1}\langle \Psi | \hat{W}_0 | \Psi \rangle$ let us consider an interesting corollary to the result obtained. When the wavefunction Ψ is expanded in terms of a set of functions $|\chi\rangle$ as in equation (B1) in Appendix B, equation (24) yields equation (25) for the matrix representation in terms of the set of functions $|\chi\rangle$ (see Appendix B).

$$\mathbf{W}_1' = \mathbf{W}_0' \mathbf{T}^{-1} \mathbf{W}_0'. \quad (25)$$

In equation (25), $\mathbf{W}_0'$ is the matrix of the operator $[4m^2c^2]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})V(\boldsymbol{\sigma}\cdot\mathbf{p})$, $\mathbf{T}$ is the matrix of the kinetic energy operator and $\mathbf{W}_1'$ is the matrix of the operator $\hat{W}_1' = [8m^3c^4]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})V^2(\boldsymbol{\sigma}\cdot\mathbf{p})$. In third order, one has equation (26) for the matrix of the third-order operator $\hat{W}_2' = [16m^4c^6]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})V^3(\boldsymbol{\sigma}\cdot\mathbf{p})$ in terms of the basis set $|\chi\rangle$.

$$\mathbf{W}_2' = \mathbf{W}_0' \mathbf{T}^{-1} \mathbf{W}_0' \mathbf{T}^{-1} \mathbf{W}_0'. \quad (26)$$

Thus, as follows from the first line in equation (19), the ZORA Hamiltonian matrix can be represented as in equation (27),

$$\mathbf{H}^{\mathrm{ZORA}} = \mathbf{T} + \mathbf{V} + \mathbf{W}' , \tag{27}$$

where $\mathbf{W}'$ is given by equation (28)

$$\begin{aligned}\mathbf{W}' &= \mathbf{W}'_0 + \mathbf{W}'_0\mathbf{T}^{-1}\mathbf{W}'_0 + \mathbf{W}'_0\mathbf{T}^{-1}\mathbf{W}'_0\mathbf{T}^{-1}\mathbf{W}'_0 + \cdots \\ &= \mathbf{W}'_0 + \mathbf{W}'_0\mathbf{T}^{-1}\mathbf{W}'. \end{aligned} \tag{28}$$

Equation (28) was obtained in [10, 11] in a completely different way where the use of a spectral resolution of the identity with the help of a kinetically balanced basis set [23] was made. However, the analysis presented above demonstrates that equation (28) represents in fact a perturbation expansion in terms of the free-particle solutions of the non-relativistic equation summed to all orders in the potential V. This perturbation expansion takes only the leading relativistic corrections such as those given in equations (16) and (17), and (20) and (21) into account.

2.4. *Anatomy of the lowest-order correction*

Let us now estimate the lowest-order relativistic correction represented by the expectation value of the operator $\hat{W}'_0 = [4m^2c^2]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})V(\boldsymbol{\sigma}\cdot\mathbf{p})$. Using the Dirac relationship (29) [5]

$$(\boldsymbol{\sigma}\cdot\mathbf{a})(\boldsymbol{\sigma}\cdot\mathbf{b}) = \mathbf{a}\cdot\mathbf{b} + \mathrm{i}\boldsymbol{\sigma}\cdot(\mathbf{a}\times\mathbf{b}) \tag{29}$$

the expectation value of $\hat{W}'_0$ can be represented as in equation (30).

$$\langle\Psi|\hat{W}'_0|\Psi\rangle = \frac{1}{4m^2c^2}\langle\Psi|\mathbf{p}V\cdot\mathbf{p}|\Psi\rangle + \frac{\mathrm{i}}{4m^2c^2}\langle\Psi|\boldsymbol{\sigma}\cdot(\mathbf{p}V\times\mathbf{p})|\Psi\rangle. \tag{30}$$

The second term in equation (30) is the well-known spin–orbit term and the first term on the right-hand side with the help of equation (31)

$$\mathbf{p}V\cdot\mathbf{p}\Psi = \frac{1}{2}\mathbf{p}^2V\Psi + \frac{1}{2}V\mathbf{p}^2\Psi - \frac{1}{2}\left(\mathbf{p}^2V\right)\Psi \tag{31}$$

can be written according to equation (32)

$$\begin{aligned}\frac{1}{4m^2c^2}\langle\Psi|\mathbf{p}V\cdot\mathbf{p}|\Psi\rangle &= \frac{1}{8m^2c^2}\langle\Psi|\mathbf{p}^2V + V\mathbf{p}^2|\Psi\rangle \\ &\quad - \frac{1}{8m^2c^2}\langle\Psi|\left(\mathbf{p}^2V\right)|\Psi\rangle \\ &= \frac{1}{4mc^2}\langle\Psi|[\hat{T}, V]_+|\Psi\rangle \\ &\quad - \frac{1}{8m^2c^2}\langle\Psi|\left(\mathbf{p}^2V\right)|\Psi\rangle. \end{aligned} \tag{32}$$

In equation (32) the last term on the right-hand side is the Darwin term [7] and the first term is an anticommutator of the non-relativistic kinetic energy operator and the potential. Assuming that Ψ is an eigenfunction of the non-relativistic Hamiltonian with the corresponding eigenvalue E, the expectation value of the anticommutator on the right-hand side of equation (32) can be estimated as in equation (33):

$$\begin{aligned}\langle\Psi|[\hat{T}, V]_+|\Psi\rangle &= \langle\Psi|\hat{H}^2 - \hat{T}^2 - V^2|\Psi\rangle \\ &= E^2 - \langle\Psi|\hat{T}^2|\Psi\rangle - \langle\Psi|V^2|\Psi\rangle \\ &= 2tv - \left(\langle\Psi|\hat{T}^2|\Psi\rangle - t^2\right) - \left(\langle\Psi|V^2|\Psi\rangle - v^2\right) \\ &= 2tv - \Delta t^2 - \Delta v^2. \end{aligned} \tag{33}$$

In equation (33), t and v are the expectation values of the non-relativistic kinetic energy and the potential energy, respectively. Now let us note that the two differences, Δt^2 and Δv^2, are equal, that is $\Delta t^2 = \Delta v^2$ for a solution of the Schrödinger equation (see Appendix C). Thus, equation (33) can be rewritten according to equation (34),

$$\begin{aligned}\langle\Psi|[\hat{T}, V]_+|\Psi\rangle &= 2tv - 2\Delta t^2 = 2tv - 2\left(\langle\Psi|\hat{T}^2|\Psi\rangle - t^2\right) \\ &= tv - 2\langle\Psi|\hat{T}^2|\Psi\rangle \\ &= tv - \left\langle\Psi\left|\frac{\mathbf{p}^4}{2m^2}\right|\Psi\right\rangle, \end{aligned} \tag{34}$$

where the use of the non-relativistic virial theorem ($v = -2t$) was made. Substituting equation (34) into equation (32) and using equation (30), one obtains equation (35)

$$\begin{aligned}\langle\Psi|\hat{W}'_0|\Psi\rangle &= \frac{tv}{4mc^2} - \frac{1}{8m^3c^2}\langle\Psi|\mathbf{p}^4|\Psi\rangle - \frac{1}{8m^2c^2}\langle\Psi|\left(\mathbf{p}^2V\right)|\Psi\rangle \\ &\quad + \frac{\mathrm{i}}{4m^2c^2}\langle\Psi|\boldsymbol{\sigma}\cdot(\mathbf{p}V\times\mathbf{p})|\Psi\rangle, \end{aligned} \tag{35}$$

which is valid for any non-relativistic wavefunction Ψ. If t and v are small quantities, which is true for valence and sub-valence electrons in atoms and molecules, the first term in equation (35) can be neglected and the well-known result [7] of the Pauli perturbation theory is recovered. For large energies, for example for deep energy levels in the atomic core region, the first term in equation (35) is non-negligible. For attractive Coulomb potential, this term makes a large negative contribution which is comparable in magnitude with the mass–velocity and Darwin terms in equation (35).

3. Conclusions

By expanding the Dirac equation [5] transformed to a Foldy–Wouthuysen representation [16] near the

free-particle solution, it has been demonstrated that the ZORA Hamiltonian [1–4] is a result of an infinite summation of the leading relativistic corrections to the free-particle non-relativistic energy. This conclusion helps to draw an analogy between the zeroth-order regular approximation and the random-phase approximation (RPA) [24] in quantum many-body theory. Indeed, the two approaches, ZORA and RPA, take infinite-order summation of those terms in the complete perturbation expansion, which are non-vanishing under certain assumptions—non-relativistic limit in the case of ZORA and weak particle–particle interaction limit in the case of RPA. This is at variance with the finite-order perturbation theory, such as the Douglas–Kroll method [13–15] in relativistic theory or the Møller–Plesset method [25] in many-body theory, where all terms up to a certain (finite) order are taken from the complete perturbation series.

The first-order perturbation correction taken into account in the ZORA Hamiltonian, the term $[4m^2c^2]^{-1}\langle\Psi|(\boldsymbol{\sigma}\cdot\mathbf{p})V(\boldsymbol{\sigma}\cdot\mathbf{p})|\Psi\rangle$, contains all relativistic corrections from the one-electron Breit–Pauli Hamiltonian. This result is general and holds not only for hydrogen-like atomic systems, as has been demonstrated numerically by Snijders and Sadlej [20], but also for any quantum system.

The above conclusions shed light on the remarkable performance of ZORA and ZORA-related methods in atomic and molecular calculations. For the valence and sub-valence electrons, the ZORA Hamiltonian provides the closest match with the exact relativistic Hamiltonian for electronic states. This feature guarantees that all atomic and molecular properties, which depend on the valence electrons, are reproduced nearly exactly with the use of the ZORA Hamiltonian. In particular, this should translate to molecular geometries and binding energies obtained with ZORA. The current literature offers a multitude of examples illustrating the excellent performance of ZORA (and ZORA-related methods) in the calculation of molecular structure and molecular stability [6, 10, 11]. First-order response properties, such as charge distributions, dipole moments, and higher moments, etc., are reproduced reliably with the help of ZORA (and ZORA-related methods) [6, 26]. Second-order properties such as electric dipole polarizabilities or NMR chemical shifts belong also to the group of properties described accurately with the help of ZORA. It should be mentioned that the chemical shifts of heavy and superheavy atoms are dominated by the paramagnetic contribution, which in turn is dominated by the valence and sub-valence electrons. Quite recently, the excellent performance of ZORA in the calculation of NMR chemical shifts was documented in the literature [27]. The analysis presented in the present paper offers a theoretical basis for these observations. Since our analysis does not refer to a specific atomic or molecular system, the conclusions inferred are valid for a wide variety of physical problems including, for example, the relativistic quantum oscillator or the relativistic rigid rotator, for which ZORA should provide an extremely good description in the low-energy limit.

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Appendix A: Complete expressions for the relativistic corrections to the free-particle equation

Multiplying equation (13) from the left with $\Psi_{\mathrm{L}}^{(0)\dagger}$, integrating and using the complex conjugate of equation (12) one arrives at equation (A1) for the first-order correction to the free-particle energy.

$$E^{(1)} = \left\langle \Psi_{\mathrm{L}}^{(0)} | V | \Psi_{\mathrm{L}}^{(0)} \right\rangle + \left\langle \Psi_{\mathrm{L}}^{(0)} \left| \frac{c^2 \hat{W}_0}{(E^{(0)} + 2mc^2)^2} \right| \Psi_{\mathrm{L}}^{(0)} \right\rangle. \quad \text{(A1)}$$

The correction of the second order is obtained from equation (14). Upon multiplication from the left with $\Psi_{\mathrm{L}}^{(0)\dagger}$ and integration and using the complex conjugate of equation (12) one obtains equation (A2):

$$\begin{aligned}
&\left\langle \Psi_{\mathrm{L}}^{(0)} \left| V + (\boldsymbol{\sigma}\cdot\mathbf{p}) \frac{c^2((E^{(0)} + 2mc^2)V - 2E^{(0)}(E^{(1)} - V))}{(E^{(0)} + 2mc^2)^3} \right.\right. \\
&\quad \left.\left. \times (\boldsymbol{\sigma}\cdot\mathbf{p}) \right| \Psi_{\mathrm{L}}^{(1)} \right\rangle + \left\langle \Psi_{\mathrm{L}}^{(0)} \right| (\boldsymbol{\sigma}\cdot\mathbf{p}) \\
&\quad \times \left[\frac{2c^2(E^{(0)}(E^{(1)} - V)(E^{(1)} - 2V) - mc^2(E^{(1)^2} - V^2))}{(E^{(0)} + 2mc^2)^4} \right. \\
&\quad \left. - \frac{2c^2 E^{(0)} E^{(2)}}{(E^{(0)} + 2mc^2)^3} \right] (\boldsymbol{\sigma}\cdot\mathbf{p}) \left| \Psi_{\mathrm{L}}^{(0)} \right\rangle \\
&= E^{(1)} \left\langle \Psi_{\mathrm{L}}^{(0)} \left| 1 + (\boldsymbol{\sigma}\cdot\mathbf{p}) \frac{c^2}{(E^{(0)} + 2mc^2)^2} (\boldsymbol{\sigma}\cdot\mathbf{p}) \right| \Psi_{\mathrm{L}}^{(1)} \right\rangle \\
&\quad + E^{(2)} \left\langle \Psi_{\mathrm{L}}^{(0)} \left| 1 + (\boldsymbol{\sigma}\cdot\mathbf{p}) \frac{c^2}{(E^{(0)} + 2mc^2)^2} (\boldsymbol{\sigma}\cdot\mathbf{p}) \right| \Psi_{\mathrm{L}}^{(0)} \right\rangle \\
&\quad - E^{(0)} \left\langle \Psi_{\mathrm{L}}^{(0)} \left| (\boldsymbol{\sigma}\cdot\mathbf{p}) \frac{2c^2(E^{(1)} - V)}{(E^{(0)} + 2mc^2)^3} (\boldsymbol{\sigma}\cdot\mathbf{p}) \right| \Psi_{\mathrm{L}}^{(1)} \right\rangle \\
&\quad - E^{(1)} \left\langle \Psi_{\mathrm{L}}^{(0)} \left| (\boldsymbol{\sigma}\cdot\mathbf{p}) \frac{2c^2(E^{(1)} - V)}{(E^{(0)} + 2mc^2)^3} (\boldsymbol{\sigma}\cdot\mathbf{p}) \right| \Psi_{\mathrm{L}}^{(0)} \right\rangle \\
&\quad + E^{(0)} \left\langle \Psi_{\mathrm{L}}^{(0)} \left| (\boldsymbol{\sigma}\cdot\mathbf{p}) \frac{c^2(3(E^{(1)} - V)^2 - 2E^{(2)}(E^{(0)} + 2mc^2))}{(E^{(0)} + 2mc^2)^4} \right.\right. \\
&\quad \left.\left. \times (\boldsymbol{\sigma}\cdot\mathbf{p}) \right| \Psi_{\mathrm{L}}^{(0)} \right\rangle. \quad \text{(A2)}
\end{aligned}$$

For the purpose of transforming equation (A2) into a more convenient form, equation (A3) is used, which is obtained from equation (13) by taking its complex conjugate, multiplying with $\Psi_{\mathrm{L}}^{(1)}$ from the right and integrating:

$$\begin{aligned}
&\left\langle \Psi_{\mathrm{L}}^{(1)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(0)}+mc^2)}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}) \right. \\
&\quad \left. - E^{(0)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right) \middle| \Psi_{\mathrm{L}}^{(1)} \right\rangle \\
&= E^{(1)}\left\langle \Psi_{\mathrm{L}}^{(0)} \middle| 1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}) \middle| \Psi_{\mathrm{L}}^{(1)} \right\rangle \\
&\quad - E^{(0)}\left\langle \Psi_{\mathrm{L}}^{(0)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(1)}-V)}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p}) \middle| \Psi_{\mathrm{L}}^{(1)} \right\rangle \\
&\quad - \left\langle \Psi_{\mathrm{L}}^{(0)} \middle| V+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2((E^{(0)}+2mc^2)V-2E^{(0)}(E^{(1)}-V))}{(E^{(0)}+2mc^2)^3} \right. \\
&\quad \left. \times(\boldsymbol{\sigma}\cdot\mathbf{p}) \right) \middle| \Psi_{\mathrm{L}}^{(1)} \Big\rangle. \qquad \text{(A3)}
\end{aligned}$$

Thus, equation (A2) transforms to equation (A4),

$$\begin{aligned}
&\left\langle \Psi_{\mathrm{L}}^{(0)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p}) \right. \\
&\quad \times \left[\frac{2c^2(E^{(0)}(E^{(1)}-V)(E^{(1)}-2V)-mc^2({E^{(1)}}^2-V^2))}{(E^{(0)}+2mc^2)^4} \right. \\
&\quad \left. \left. -\frac{2c^2E^{(0)}E^{(2)}}{(E^{(0)}+2mc^2)^3} \right](\boldsymbol{\sigma}\cdot\mathbf{p}) \middle| \Psi_{\mathrm{L}}^{(0)} \right\rangle \\
&= E^{(2)} - E^{(1)}\left\langle \Psi_{\mathrm{L}}^{(0)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(1)}-V)}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p}) \middle| \Psi_{\mathrm{L}}^{(0)} \right\rangle \\
&\quad + E^{(0)}\left\langle \Psi_{\mathrm{L}}^{(0)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2(3(E^{(1)}-V)^2-2E^{(2)}(E^{(0)}+2mc^2))}{(E^{(0)}+2mc^2)^4} \right. \\
&\quad \left. \times(\boldsymbol{\sigma}\cdot\mathbf{p}) \middle| \Psi_{\mathrm{L}}^{(0)} \right\rangle + \left\langle \Psi_{\mathrm{L}}^{(1)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(0)}+mc^2)}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}) \right. \\
&\quad \left. - E^{(0)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right) \middle| \Psi_{\mathrm{L}}^{(1)} \right\rangle, \qquad \text{(A4)}
\end{aligned}$$

which after some algebra, transforms to equation (A5) for the second-order correction to the free-particle relativistic energy.

$$\begin{aligned}
E^{(2)} &= \left\langle \Psi_{\mathrm{L}}^{(0)} \middle| \frac{c^2(\hat{W}_1 - 2E^{(1)}\hat{W}_0)}{(E^{(0)}+2mc^2)^3} \middle| \Psi_{\mathrm{L}}^{(0)} \right\rangle \\
&\quad + {E^{(1)}}^2\left\langle \Psi_{\mathrm{L}}^{(0)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^3}(\boldsymbol{\sigma}\cdot\mathbf{p}) \middle| \Psi_{\mathrm{L}}^{(0)} \right\rangle \\
&\quad - \left\langle \Psi_{\mathrm{L}}^{(1)} \middle| (\boldsymbol{\sigma}\cdot\mathbf{p})\frac{2c^2(E^{(0)}+mc^2)}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p}) \right. \\
&\quad \left. - E^{(0)}\left(1+(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(E^{(0)}+2mc^2)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})\right) \middle| \Psi_{\mathrm{L}}^{(1)} \right\rangle. \qquad \text{(A5)}
\end{aligned}$$

In the non-relativistic limit, i.e. $E^{(0)} \ll mc^2$, $E^{(1)} \ll mc^2$, $E^{(2)} \ll mc^2$, equations (A1) and (A5) lead to equations (20) and (21).

Appendix B: Basis set expansion

Let us expand an arbitrary one-electron wavefunction Ψ_i in terms a set of functions $|\chi\rangle$ according to equation (B1)

$$\Psi_i = |\chi\rangle\mathbf{C}_i, \qquad \text{(B1)}$$

where $|\chi\rangle$ is a row vector of functions and $\mathbf{C}_i$ is a column vector of expansion coefficients. The expansion coefficients satisfy the relationship (B2),

$$\mathbf{C}_i^{\dagger}\mathbf{S}\mathbf{C}_i = \mathbf{I}, \qquad \text{(B2)}$$

(**I**: identity matrix), which implies equation (B3),

$$\mathbf{C}_i^{\dagger -1} = \mathbf{S}\mathbf{C}_i, \qquad \text{(B3}a\text{)}$$

$$\mathbf{C}_i{}^{-1} = \mathbf{C}_i^{\dagger}\mathbf{S}, \qquad \text{(B3}b\text{)}$$

$$\mathbf{C}_i\mathbf{C}_i^{\dagger} = \mathbf{S}^{-1}, \qquad \text{(B3}c\text{)}$$

where **S** is the overlap matrix, $\mathbf{S}_{\mu\nu} = \langle\chi_\mu|\chi_\nu\rangle$. Then, the energy eigenvalues E_k in equation (24) can be written as in equation (B4)

$$E_k = \langle\Psi_k|\hat{T}|\Psi_k\rangle = \mathbf{C}_k^{\dagger}\mathbf{T}\mathbf{C}_k \qquad \text{(B4)}$$

and the inverse value of E_k can be written as in equation (B5),

$$E_k{}^{-1} = \langle\Psi_k|\hat{T}|\Psi_k\rangle^{-1} = \mathbf{C}_k{}^{-1}\mathbf{T}^{-1}\mathbf{C}_k^{\dagger -1} = \mathbf{C}_k^{\dagger}\mathbf{S}\mathbf{T}^{-1}\mathbf{S}\mathbf{C}_k, \qquad \text{(B5)}$$

where the use of equation (B3) was made. Substituting equation (B5) into equation (24) and using equation

(B1) one has equation (B6),

$$\frac{1}{8m^3c^4}\langle\Psi_i|\hat{W}_1|\Psi_i\rangle = \sum_k \mathbf{C}_i^\dagger \mathbf{W}_0' \mathbf{C}_k \mathbf{C}_k^\dagger \mathbf{S}\mathbf{T}^{-1}\mathbf{S}\mathbf{C}_k\mathbf{C}_k^\dagger \mathbf{W}_0'\mathbf{C}_i$$
$$= \mathbf{C}_i^\dagger(\mathbf{W}_0'\mathbf{T}^{-1}\mathbf{W}_0')\mathbf{C}_i, \qquad \text{(B6)}$$

which leads to equation (25) in the text. In equations (B4), (B5) and (B6), $\mathbf{W}_0'$ and $\mathbf{T}$ are the matrices of the operator $[4m^2c^2]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})V(\boldsymbol{\sigma}\cdot\mathbf{p})$ and the kinetic energy operator, respectively. $\mathbf{W}_0'$ is the matrix of the operator $\hat{W}_1' = [8m^3c^4]^{-1}(\boldsymbol{\sigma}\cdot\mathbf{p})V^2(\boldsymbol{\sigma}\cdot\mathbf{p})$.

Appendix C: Proof that $\langle\Psi|\hat{T}^2|\Psi\rangle - t^2 = \langle\Psi|V^2|\Psi\rangle - v^2$

Let us assume that Ψ is a solution to the Schrödinger equation (C1)

$$\left(\hat{T}+V\right)\Psi = E\Psi. \qquad \text{(C1)}$$

Then, multiplying equation (C1) with $\Psi^\dagger\hat{T}$ from the left and integrating one has equation (C2),

$$\langle\Psi|\hat{T}^2 + \hat{T}V|\Psi\rangle = (t+v)t, \qquad \text{(C2)}$$

where t and v are the expectation values of the kinetic energy operator and the potential energy, respectively. Analogously, multiplying equation (C1) with $\Psi^\dagger V$ from the left and integrating one has equation (C3),

$$\langle\Psi|V\hat{T} + V^2|\Psi\rangle = (t+v)v. \qquad \text{(C3)}$$

Subtracting equation (C3) from equation (C2) one arrives at equation (C4).

$$\left(\langle\Psi|\hat{T}^2|\Psi\rangle - t^2\right) - \left(\langle\Psi|V^2|\Psi\rangle - v^2\right) = \left\langle\Psi\middle|\left[V,\hat{T}\right]\middle|\Psi\right\rangle. \qquad \text{(C4)}$$

The expectation value of the commutator on the right-hand side of equation (C4) is zero, which follows from the hermiticity property of the kinetic and potential energy operators and from their real definiteness. Thus, equation (C4) proves the statement that $\langle\Psi|\hat{T}^2|\Psi\rangle - t^2 = \langle\Psi|V^2|\Psi\rangle - v^2$.

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