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Analogs of the Hellmann–Feynman theorem in the R-matrix theory

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Abstract

Analogs of the Hellmann–Feynman theorem are derived for eigenvalues of nonrelativistic and relativistic R-matrices and their inverses in a case of a charged particle moving in static electric and magnetic fields. The theorems relate derivatives of the eigenvalues with respect to some scalar parameter λ, on which the operator $\hat{\mathcal{H}} - E$ depends (here $\hat{\mathcal{H}}$ is either the Schrödinger or the Dirac Hamiltonian of the particle and E is the real energy), to a matrix element of $\partial[\hat{\mathcal{H}} - E]/\partial\lambda$. As an illustration of the utility of the results derived, we show that between their poles eigenvalues of nonrelativistic and relativistic R-matrices (and their inverses) are monotonic functions of energy E. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In its general form, the Hellmann–Feynman theorem [1] states that if $\hat{\mathcal{M}}$ and $\hat{\mathcal{N}}$ are operators which depend on some scalar parameter λ and if μ_n and ψ_n are, respectively, a discrete eigenvalue and an associated eigenvector to the eigenproblem

$$\hat{\mathcal{M}}\psi_n = \mu_n \hat{\mathcal{N}}\psi_n, \tag{1}$$

then, provided $\hat{\mathcal{M}}$ and $\hat{\mathcal{N}}$ are Hermitian with respect to a scalar product $\langle\langle\ |\ \rangle\rangle$, it holds

$$\frac{\partial \mu_n}{\partial\lambda} = \frac{\langle\langle\psi_n|(\partial\hat{\mathcal{M}}/\partial\lambda)\psi_n\rangle\rangle}{\langle\langle\psi_n|\hat{\mathcal{N}}\psi_n\rangle\rangle} - \mu_n \frac{\langle\langle\psi_n|(\partial\hat{\mathcal{N}}/\partial\lambda)\psi_n\rangle\rangle}{\langle\langle\psi_n|\hat{\mathcal{N}}\psi_n\rangle\rangle}. \tag{2}$$

A proof of relation (2) is trivial. In fact, the relation is so simple that it hardly deserves to be called a 'theorem'. Yet, despite its simplicity, the Hellmann–Feynman theorem, with $\hat{\mathcal{M}}$, $\hat{\mathcal{N}}$, and μ_n chosen to be a Hamiltonian of a physical system, the unit operator, and a discrete eigenenergy, respectively, has been proved to be extremely useful

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in atomic, molecular, liquid state and solid state physics, i.e., in those branches of the theory of the matter where molecular forces play the dominant role [2]. It has found applications also in other physical disciplines [2] and in the theory of special functions [3].

In this Letter we investigate the Hellmann–Feynman theorem in the context of the R-matrix theory [4] reformulated, both for the Schrödinger and Dirac particles, in the natural and convenient language of integral operators. The utility of results obtained in the course of this investigation is illustrated by showing that, both in the nonrelativistic and relativistic theories, eigenvalues of R-matrices are monotonic functions of energy.

2. The nonrelativistic case

2.1. Operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$

Throughout this Letter we shall be concerned with a finite volume $\mathcal{V}$ enclosed by a sufficiently smooth fictitious surface $\mathcal{S}$. A position vector, relative to some reference origin, of a point in the volume $\mathcal{V}$ will be denoted by $\mathbf{r}$. If the point is located on the surface $\mathcal{S}$, the position vector will be marked with $\boldsymbol{\rho}$. A unit outward vector normal to the surface $\mathcal{S}$ at the point $\boldsymbol{\rho}$ will be denoted by $\mathbf{n}(\boldsymbol{\rho})$. If $\Phi(\mathbf{r})$ and $\Phi'(\mathbf{r})$ are any two sufficiently regular functions, their scalar products over $\mathcal{V}$ and $\mathcal{S}$ are defined as

$$\langle\Phi|\Phi'\rangle = \int_{\mathcal{V}} d^3\mathbf{r}\, \Phi^*(\mathbf{r})\Phi'(\mathbf{r}), \tag{3}$$

$$(\Phi|\Phi') = \oint_{\mathcal{S}} d^2\boldsymbol{\rho}\, \Phi^*(\boldsymbol{\rho})\Phi'(\boldsymbol{\rho}), \tag{4}$$

respectively. Here $d^3\mathbf{r}$ is an infinitesimal volume element around the point $\mathbf{r}$, $d^2\boldsymbol{\rho}$ is an infinitesimal *scalar* surface element of $\mathcal{S}$ around the point $\boldsymbol{\rho}$, and the asterisk denotes complex conjugation.

The 'minimal-coupling' Schrödinger Hamiltonian for a nonrelativistic particle of mass m and electric charge q moving in static electric and magnetic fields, derivable from the real scalar potential $\phi(\mathbf{r})$ and the real vector potential $\mathbf{A}(\mathbf{r})$, respectively, is

$$\hat{\mathcal{H}} = \frac{1}{2m}\big[-\mathrm{i}\hbar\boldsymbol{\nabla} - q\mathbf{A}(\mathbf{r})\big]^2 + q\phi(\mathbf{r}). \tag{5}$$

In later parts of this section, we shall twice make use of the following, easily verifiable, integral identity

$$\big([\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Phi\big|\Phi'\big) - \big(\Phi\big|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Phi'\big) = \frac{2m}{\hbar^2}\big\langle\Phi\big|\big[\hat{\mathcal{H}} - E\big]\Phi'\big\rangle - \frac{2m}{\hbar^2}\big\langle\big[\hat{\mathcal{H}} - E\big]\Phi\big|\Phi'\big\rangle, \tag{6}$$

where $E \in \mathbb{R}$ and

$$\nabla_\perp\Phi(\boldsymbol{\rho}) = \mathbf{n}(\boldsymbol{\rho})\cdot\boldsymbol{\nabla}\Phi(\boldsymbol{\rho}), \qquad A_\perp(\boldsymbol{\rho}) = \mathbf{n}(\boldsymbol{\rho})\cdot\mathbf{A}(\boldsymbol{\rho}), \tag{7}$$

obeyed by Hamiltonian (5) and by any two sufficiently regular and otherwise arbitrary functions $\Phi(\mathbf{r})$ and $\Phi'(\mathbf{r})$ defined in $\mathcal{V}$ and on $\mathcal{S}$. Identity (6) may be viewed as a generalization of Green's integration theorem.

Consider now the situation when the particle characterized by Hamiltonian (5) moves with a prescribed energy E in the volume $\mathcal{V}$. The time-independent Schrödinger equation describing this situation is

$$\big[\hat{\mathcal{H}} - E\big]\Psi(E,\mathbf{r}) = 0. \tag{8}$$

We define a linear integral operator $\hat{\mathcal{B}}(E)$, operating in the space of functions defined on $\mathcal{S}$, so that for any solution $\Psi(E,\mathbf{r})$ to the Schrödinger equation (8) at the energy E one has

$$\big[\nabla_\perp - \mathrm{i}qA_\perp(\boldsymbol{\rho})/\hbar\big]\Psi(E,\boldsymbol{\rho}) = \hat{\mathcal{B}}(E)\Psi(E,\boldsymbol{\rho}). \tag{9}$$

We shall show that the operator $\hat{\mathcal{B}}(E)$ is Hermitian under the surface scalar product (4). To this end, we make use of identity (6) with

$$\Phi(\mathbf{r}) = \Psi(E,\mathbf{r}), \qquad \Phi'(\mathbf{r}) = \Psi'(E,\mathbf{r}), \tag{10}$$

where $\Psi(E,\mathbf{r})$ and $\Psi'(E,\mathbf{r})$ are two, possibly different, solutions to the Schrödinger equation (8) *at the same energy* E. In virtue of Eq. (8), the right side of the resulting equation vanishes and we have

$$\big([\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi\big|\Psi'\big) - \big(\Psi\big|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi'\big) = 0, \tag{11}$$

which, in conjunction with definition (9), proves the Hermitian property of $\hat{\mathcal{B}}(E)$ on the domain of solutions to the Schrödinger equation (8). Next, we define the operator $\hat{\mathcal{R}}(E)$ reciprocal to $\hat{\mathcal{B}}(E)$, i.e., satisfying

$$\hat{\mathcal{B}}(E)\hat{\mathcal{R}}(E) = \hat{\mathcal{R}}(E)\hat{\mathcal{B}}(E) = \hat{\mathcal{I}}, \tag{12}$$

where $\hat{\mathcal{I}}$ denotes the unit operator. Clearly, since $\hat{\mathcal{B}}(E)$ is Hermitian, $\hat{\mathcal{R}}(E)$ is also Hermitian. With the operator $\hat{\mathcal{R}}(E)$, the boundary relation (9) may be rewritten as

$$\Psi(E,\boldsymbol{\rho}) = \hat{\mathcal{R}}(E)\big[\nabla_\perp - \mathrm{i}qA_\perp(\boldsymbol{\rho})/\hbar\big]\Psi(E,\boldsymbol{\rho}). \tag{13}$$

Matrix representations of the operators $\hat{\mathcal{R}}(E)$ and $\hat{\mathcal{B}}(E)$ in any basis spanning the space of functions defined on $\mathcal{S}$ are an R-matrix $\mathsf{R}(E)$ and a generalized log-derivative matrix $\mathsf{B}(E)$, respectively, for Hamiltonian (5).

Kernels of the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ may be constructed from solutions to the eigenproblems

$$\hat{\mathcal{B}}(E)\Psi_n(E,\boldsymbol{\rho}) = b_n(E)\Psi_n(E,\boldsymbol{\rho}), \tag{14}$$

$$\hat{\mathcal{R}}(E)\Psi_n(E,\boldsymbol{\rho}) = b_n^{-1}(E)\Psi_n(E,\boldsymbol{\rho}), \tag{15}$$

where $\{b_n^{\pm 1}(E)\}$ are real eigenvalues and $\{\Psi_n(E,\boldsymbol{\rho})\}$ are corresponding eigenfunctions (since $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ are reciprocal, they have a common set of eigenfunctions and reciprocal spectra). Because, due to the Hermitian property of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$, eigenfunctions belonging to different eigenvalues are automatically orthogonal under the surface scalar product (4) while those associated with degenerate eigenvalues (if there are any) may always be orthogonalized, without any loss of generality we may assume that the eigenfunctions $\{\Psi_n(E,\boldsymbol{\rho})\}$ form an orthogonal set in the sense of

$$(\Psi_n|\Psi_{n'}) = 0 \quad (n \neq n'). \tag{16}$$

With these orthogonal eigenfunctions, the spectral expansions of the kernels of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ are

$$\mathcal{B}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_n \frac{\Psi_n(E,\boldsymbol{\rho})b_n(E)\Psi_n^*(E,\boldsymbol{\rho}')}{(\Psi_n|\Psi_n)}, \tag{17}$$

$$\mathcal{R}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_n \frac{\Psi_n(E,\boldsymbol{\rho})b_n^{-1}(E)\Psi_n^*(E,\boldsymbol{\rho}')}{(\Psi_n|\Psi_n)}. \tag{18}$$

2.2. *Analogs of the Hellmann–Feynman theorem for eigenvalues of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$*

Let us assume that the operator $\hat{\mathcal{H}} - E$ depends on some scalar parameter λ. Obviously, then the operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$ also are λ-dependent and in these particular cases when eigenequations (14) and (15) are identified with Eq. (1), the Hellmann–Feynman theorem (2) gives

$$\frac{\partial b_n(E)}{\partial\lambda} = \frac{(\Psi_n|(\partial\hat{\mathcal{B}}/\partial\lambda)\Psi_n)}{(\Psi_n|\Psi_n)}, \tag{19}$$

$$\frac{\partial b_n^{-1}(E)}{\partial\lambda} = \frac{(\Psi_n|(\partial\hat{\mathcal{R}}/\partial\lambda)\Psi_n)}{(\Psi_n|\Psi_n)}. \tag{20}$$

We observe that these formulas, although correct, are of no practical use since neither $\hat{\mathcal{B}}(E)$ nor $\hat{\mathcal{R}}(E)$ are known in closed forms; on employing the spectral expansions (17) and (18) in the right sides of Eqs. (19) and (20), respectively, after simple transformations we obtain nothing but trivial identities.

To derive more suitable analogs of the Hellmann–Feynman theorem for eigenvalues of $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$, we observe that, due to definition (9), eigenequation (14) may be rewritten as

$$\big[\nabla_\perp - \mathrm{i}qA_\perp(\boldsymbol{\rho})/\hbar\big]\Psi_n(E,\boldsymbol{\rho}) = b_n(E)\Psi_n(E,\boldsymbol{\rho}), \tag{21}$$

hence, the particular eigenvalue $b_n(E)$ of $\hat{\mathcal{B}}(E)$ may be obtained from the formula

$$b_n(E) = \frac{(\Psi_n|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n)}{(\Psi_n|\Psi_n)}. \tag{22}$$

Differentiating both sides of Eq. (22) with respect to the parameter λ and employing Eq. (21) yields

$$\frac{\partial b_n(E)}{\partial\lambda} = \frac{(\Psi_n|(\partial[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n/\partial\lambda)) - b_n(E)(\Psi_n|(\partial\Psi_n/\partial\lambda))}{(\Psi_n|\Psi_n)}. \tag{23}$$

To transform the numerator in the fraction on the right side of the above equation, we make use of the generalized Green's identity (6) with

$$\Phi(\mathbf{r}) = \Psi_n(E,\mathbf{r}), \qquad \Phi'(\mathbf{r}) = \frac{\partial\Psi_n(E,\mathbf{r})}{\partial\lambda} \tag{24}$$

and, in virtue of the Schrödinger equation (8) and the boundary condition (21), obtain

$$b_n(E)\left(\Psi_n\middle|\frac{\partial\Psi_n}{\partial\lambda}\right) - \left(\Psi_n\middle|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\frac{\partial\Psi_n}{\partial\lambda}\right) = \frac{2m}{\hbar^2}\left\langle\Psi_n\middle|\big[\hat{\mathcal{H}} - E\big]\frac{\partial\Psi_n}{\partial\lambda}\right\rangle. \tag{25}$$

Both sides of Eq. (25) may be further transformed if we exploit the identities

$$\left(\Psi_n\middle|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\frac{\partial\Psi_n}{\partial\lambda}\right) = \left(\Psi_n\middle|\frac{\partial[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n}{\partial\lambda}\right) - \left(\Psi_n\middle|\frac{\partial[-\mathrm{i}qA_\perp/\hbar]}{\partial\lambda}\Psi_n\right) \tag{26}$$

and

$$\left\langle\Psi_n\middle|\big[\hat{\mathcal{H}} - E\big]\frac{\partial\Psi_n}{\partial\lambda}\right\rangle = \left\langle\Psi_n\middle|\frac{\partial[\hat{\mathcal{H}} - E]\Psi_n}{\partial\lambda}\right\rangle - \left\langle\Psi_n\middle|\frac{\partial[\hat{\mathcal{H}} - E]}{\partial\lambda}\Psi_n\right\rangle, \tag{27}$$

and notice the fact that the first term on the right of Eq. (27) vanishes because of the Schrödinger equation (8). This yields

$$\left(\Psi_n\middle|\frac{\partial[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n}{\partial\lambda}\right) - b_n(E)\left(\Psi_n\middle|\frac{\partial\Psi_n}{\partial\lambda}\right) = \left(\Psi_n\middle|\frac{\partial[-\mathrm{i}qA_\perp/\hbar]}{\partial\lambda}\Psi_n\right) + \frac{2m}{\hbar^2}\left\langle\Psi_n\middle|\frac{\partial[\hat{\mathcal{H}} - E]}{\partial\lambda}\Psi_n\right\rangle. \tag{28}$$

On employing this result in Eq. (23), we finally arrive at the following relation for the derivative, with respect to the parameter λ, of an eigenvalue of the operator $\hat{\mathcal{B}}(E)$:

$$\frac{\partial b_n(E)}{\partial\lambda} = \frac{(\Psi_n|(\partial[-\mathrm{i}qA_\perp/\hbar]/\partial\lambda)\Psi_n)}{(\Psi_n|\Psi_n)} + \frac{2m}{\hbar^2}\frac{\langle\Psi_n|(\partial[\hat{\mathcal{H}} - E]/\partial\lambda)\Psi_n\rangle}{(\Psi_n|\Psi_n)}. \tag{29}$$

The counterpart relation for the derivative of an eigenvalue of the operator $\hat{\mathcal{R}}(E)$ is most simply obtained from the trivial identity

$$\frac{\partial b_n^{-1}(E)}{\partial\lambda} = -b_n^{-2}(E)\frac{\partial b_n(E)}{\partial\lambda} \tag{30}$$

and from Eqs. (29) and (22); one finds

$$\frac{\partial b_n^{-1}(E)}{\partial\lambda} = -\frac{(\Psi_n|(\partial[-\mathrm{i}qA_\perp/\hbar]/\partial\lambda)\Psi_n)}{([\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n)} - \frac{2m}{\hbar^2}\frac{\langle\Psi_n|(\partial[\hat{\mathcal{H}} - E]/\partial\lambda)\Psi_n\rangle}{([\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n)}. \tag{31}$$

Eqs. (29) and (31) are the sought convenient analogs of the Hellmann–Feynman theorem in the nonrelativistic R-matrix theory.

The utility of Eqs. (29) and (31) is nicely illustrated if one considers the particular case $\lambda = E$. Then Eq. (29) becomes

$$\frac{\partial b_n(E)}{\partial E} = -\frac{2m}{\hbar^2}\frac{\langle\Psi_n|\Psi_n\rangle}{(\Psi_n|\Psi_n)}. \tag{32}$$

Since the numerator in the fraction on the right side of Eq. (32) is positive and the denumerator is nonnegative (Eq. (22) shows that it vanishes at those energies at which $b_n(E)$ has poles) we infer that between their poles eigenvalues of the operator $\hat{\mathcal{B}}(E)$ are monotonically *decreasing* functions of the energy E (cf. Ref. [5]). Similarly, from Eq. (31) we obtain

$$\frac{\partial b_n^{-1}(E)}{\partial E} = \frac{2m}{\hbar^2}\frac{\langle\Psi_n|\Psi_n\rangle}{([\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n|[\nabla_\perp - \mathrm{i}qA_\perp/\hbar]\Psi_n)}, \tag{33}$$

which implies that between their poles (coinciding with zeros of the corresponding eigenvalues of the operator $\hat{\mathcal{B}}(E)$) eigenvalues of the operator $\hat{\mathcal{R}}(E)$ are monotonically *increasing* functions of the energy E.

3. The relativistic case

3.1. Operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$

In this section we shall carry out considerations analogous to those of Section 2 but for a relativistic Dirac particle. We shall adopt all the definitions given in the first paragraph of Section 2.1 apart from definitions (3) and (4) of the scalar products. The latter definitions are inappropriate in the relativistic theory, where the functions $\Phi(\mathbf{r})$ and $\Phi'(\mathbf{r})$ are four component spinors, and therefore are to be replaced by

$$\langle\Phi|\Phi'\rangle = \int_{\mathcal{V}} d^3\mathbf{r}\,\Phi^\dagger(\mathbf{r})\Phi'(\mathbf{r}), \tag{34}$$

$$(\Phi|\Phi') = \oint_{\mathcal{S}} d^2\boldsymbol{\rho}\,\Phi^\dagger(\boldsymbol{\rho})\Phi'(\boldsymbol{\rho}), \tag{35}$$

respectively, where the dagger denotes the matrix Hermitian conjugation.

The relativistic analog of the Schrödinger Hamiltonian (5) is the Dirac Hamiltonian

$$\hat{\mathcal{H}} = c\boldsymbol{\alpha}\cdot\left[-\mathrm{i}\hbar\boldsymbol{\nabla} - q\mathbf{A}(\mathbf{r})\right] + \beta mc^2 + q\phi(\mathbf{r}), \tag{36}$$

where $\boldsymbol{\alpha}$ and β are the standard 4×4 Dirac matrices [6]. For any two sufficiently regular four-component spinor functions $\Phi(\mathbf{r})$ and $\Phi'(\mathbf{r})$ the operator $\hat{\mathcal{H}} - E$, where $E \in \mathbb{R}$, obeys the integral relation

$$c\hbar(\Phi|\mathrm{i}\alpha_\perp\Phi') = \left\langle\left[\hat{\mathcal{H}} - E\right]\Phi\middle|\Phi'\right\rangle - \left\langle\Phi\middle|\left[\hat{\mathcal{H}} - E\right]\Phi'\right\rangle, \tag{37}$$

where

$$\alpha_\perp(\boldsymbol{\rho}) = \mathbf{n}(\boldsymbol{\rho})\cdot\boldsymbol{\alpha}, \tag{38}$$

which follows from the Gauss divergence theorem. We shall find it convenient to rewrite relation (37) in a different form by transforming its left side. To this end, we define the matrices

$$\alpha_\perp^{(\pm)}(\boldsymbol{\rho}) = \beta^{(\pm)}\alpha_\perp(\boldsymbol{\rho}), \qquad \beta^{(\pm)} = \frac{1}{2}(I \pm \beta) \tag{39}$$

(here I is the unit 4×4 matrix), with the conjugation properties

$$\alpha_\perp^{(\pm)\dagger}(\boldsymbol{\rho}) = \alpha_\perp^{(\mp)}(\boldsymbol{\rho}), \qquad \beta^{(\pm)\dagger} = \beta^{(\pm)}, \tag{40}$$

and decompose

$$\alpha_\perp(\boldsymbol{\rho}) = \alpha_\perp^{(+)}(\boldsymbol{\rho}) + \alpha_\perp^{(-)}(\boldsymbol{\rho}). \tag{41}$$

Substituting Eq. (41) to Eq. (37) and applying the first of the conjugation relations (40), we obtain

$$\big(\mathrm{i}\alpha_\perp^{(\pm)}\Phi\big|\Phi'\big) - \big(\Phi\big|\mathrm{i}\alpha_\perp^{(\pm)}\Phi'\big) = \frac{1}{c\hbar}\big\langle\Phi\big|\big[\hat{\mathcal{H}} - E\big]\Phi'\big\rangle - \frac{1}{c\hbar}\big\langle\big[\hat{\mathcal{H}} - E\big]\Phi\big|\Phi'\big\rangle. \tag{42}$$

We shall make use of Eq. (42) in later parts of this section.

Assume now that the considered Dirac particle moves with the prescribed total energy E (including the rest energy mc^2). The relevant time-independent Dirac equation is

$$\big[\hat{\mathcal{H}} - E\big]\Psi(E, \mathbf{r}) = 0. \tag{43}$$

For that equation we define two integral operators $\hat{\mathcal{B}}^{(\pm)}(E) = \beta^{(\pm)}\hat{\mathcal{B}}^{(\pm)}(E)\beta^{(\pm)}$, on the space of four-component spinors defined on $\mathcal{S}$, in such a manner that for any solution to Eq. (43) it holds

$$\mathrm{i}\alpha_\perp^{(\pm)}(\boldsymbol{\rho})\Psi(E, \boldsymbol{\rho}) = \gamma^{(\pm)}\hat{\mathcal{B}}^{(\pm)}(E)\Psi(E, \boldsymbol{\rho}), \tag{44}$$

where

$$\gamma^{(\pm)} = \pm\left(\frac{\hbar}{2mc}\right)^{\pm 1} \tag{45}$$

(notice the useful relationship $\gamma^{(+)}\gamma^{(-)} = -1$). The operators $\hat{\mathcal{B}}^{(\pm)}(E)$ are analogs of the operator $\hat{\mathcal{B}}(E)$ used in the nonrelativistic theory of Section 2. They are Hermitian on the domain of solutions to Eq. (43). One proves that by substituting

$$\Phi(\mathbf{r}) = \Psi(E, \mathbf{r}), \qquad \Phi'(\mathbf{r}) = \Psi'(E, \mathbf{r}), \tag{46}$$

where both $\Psi(E, \mathbf{r})$ and $\Psi'(E, \mathbf{r})$ are assumed to obey Eq. (43) at the same energy E, to identity (42). Because of the assumption, the result is

$$\big(\mathrm{i}\alpha_\perp^{(\pm)}\Psi\big|\Psi'\big) - \big(\Psi\big|\mathrm{i}\alpha_\perp^{(\pm)}\Psi'\big) = 0. \tag{47}$$

Because of definition (44), Eq. (47) may be rewritten in the form

$$\big(\hat{\mathcal{B}}^{(\pm)}\Psi\big|\Psi'\big) = \big(\Psi\big|\hat{\mathcal{B}}^{(\pm)}\Psi'\big), \tag{48}$$

which completes the proof.

The operators $\hat{\mathcal{B}}^{(\pm)}(E)$ do not have inverses in the common sense but possess generalized inverses $\hat{\mathcal{R}}^{(\pm)}(E)$, defined by

$$\hat{\mathcal{B}}^{(\pm)}(E)\hat{\mathcal{R}}^{(\pm)}(E) = \hat{\mathcal{R}}^{(\pm)}(E)\hat{\mathcal{B}}^{(\pm)}(E) = \beta^{(\pm)}\hat{\mathcal{I}}. \tag{49}$$

The operators $\hat{\mathcal{R}}^{(\pm)}(E)$ are Hermitian. In terms of them the boundary relations (44) become

$$\beta^{(\pm)}\Psi(E, \boldsymbol{\rho}) = -\gamma^{(\mp)}\hat{\mathcal{R}}^{(\pm)}(E)\mathrm{i}\alpha_\perp^{(\pm)}(\boldsymbol{\rho})\Psi(E, \boldsymbol{\rho}). \tag{50}$$

The operators $\hat{\mathcal{R}}^{(\pm)}(E)$ are analogs of the operator $\hat{\mathcal{R}}(E)$ occurring in the nonrelativistic theory. Matrix representations $\mathsf{R}^{(\pm)}(E)$ of $\hat{\mathcal{R}}^{(\pm)}(E)$ in any spinor basis on the surface $\mathcal{S}$ are relativistic R-matrices for the problem considered while matrix representations $\mathsf{B}^{(\pm)}(E)$ of $\hat{\mathcal{B}}^{(\pm)}(E)$ are analogs of the nonrelativistic generalized log-derivative matrix $\mathsf{B}(E)$.

Let us now consider a subset $\{\Psi_n(E,\mathbf{r})\}$ of those solutions to the Dirac equation which on the surface $\mathcal{S}$ obey the boundary conditions

$$\mathrm{i}\alpha_\perp^{(+)}(\boldsymbol{\rho})\Psi_n(E,\boldsymbol{\rho}) = \gamma^{(+)}b_n(E)\beta^{(+)}\Psi_n(E,\boldsymbol{\rho}), \tag{51}$$

with the constants $\{b_n(E)\}$ not known in advance. Premultiplying Eq. (51) from the left by $\alpha_\perp^{(-)}(\boldsymbol{\rho})$ and making use of the well-known commutation and anticommutation relations satisfied by the Dirac matrices $\boldsymbol{\alpha}$ and β [6], after some simple manipulations we transform Eq. (51) to the form

$$\mathrm{i}\alpha_\perp^{(-)}(\boldsymbol{\rho})\Psi_n(E,\boldsymbol{\rho}) = \gamma^{(-)}b_n^{-1}(E)\beta^{(-)}\Psi_n(E,\boldsymbol{\rho}). \tag{52}$$

We see that Eqs. (51) and (52) may be rewritten compactly as

$$\mathrm{i}\alpha_\perp^{(\pm)}(\boldsymbol{\rho})\Psi_n(E,\boldsymbol{\rho}) = \gamma^{(\pm)}b_n^{\pm 1}(E)\beta^{(\pm)}\Psi_n(E,\boldsymbol{\rho}). \tag{53}$$

Because $\{\Psi_n(E,\mathbf{r})\}$ are solutions to the Dirac equation (43), apart from Eq. (53) they satisfy also Eqs. (44) and (50). On combining these three equations, we find

$$\hat{\mathcal{B}}^{(\pm)}(E)\Psi_n(E,\boldsymbol{\rho}) = b_n^{\pm 1}(E)\beta^{(\pm)}\Psi_n(E,\boldsymbol{\rho}), \tag{54}$$

$$\hat{\mathcal{R}}^{(\pm)}(E)\Psi_n(E,\boldsymbol{\rho}) = b_n^{\mp 1}(E)\beta^{(\pm)}\Psi_n(E,\boldsymbol{\rho}), \tag{55}$$

i.e., the surface functions $\{\Psi_n(E,\boldsymbol{\rho})\}$ are simultaneous eigenfunctions of the four operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$, with the singular weights $\beta^{(\pm)}$, while the constants $\{b_n^{\pm 1}(E)\}$ are associated eigenvalues.

Since $\hat{\mathcal{B}}^{(\pm)}(E)$, $\hat{\mathcal{R}}^{(\pm)}(E)$, and $\beta^{(\pm)}$ are Hermitian, the eigenvalues $\{b_n^{\pm 1}(E)\}$ are real and the eigenfunctions $\{\Psi_n(E,\boldsymbol{\rho})\}$ may be chosen to satisfy *simultaneously* the following *two* orthogonality relations

$$\big(\Psi_n\big|\beta^{(\pm)}\Psi_{n'}\big) = 0 \quad (n \neq n'). \tag{56}$$

With eigenfunctions orthogonalized in such a manner, spectral expansions of the kernels of $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$ are

$$\mathcal{B}^{(\pm)}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_n \frac{\beta^{(\pm)}\Psi_n(E,\boldsymbol{\rho})b_n^{\pm 1}(E)\Psi_n^\dagger(E,\boldsymbol{\rho}')\beta^{(\pm)}}{(\Psi_n|\beta^{(\pm)}\Psi_n)}, \tag{57}$$

$$\mathcal{R}^{(\pm)}(E,\boldsymbol{\rho},\boldsymbol{\rho}') = \sum_n \frac{\beta^{(\pm)}\Psi_n(E,\boldsymbol{\rho})b_n^{\mp 1}(E)\Psi_n^\dagger(E,\boldsymbol{\rho}')\beta^{(\pm)}}{(\Psi_n|\beta^{(\pm)}\Psi_n)}. \tag{58}$$

3.2. Analogs of the Hellmann–Feynman theorem for eigenvalues of $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$

Presume that the operator $\hat{\mathcal{H}} - E$, with $\hat{\mathcal{H}}$ defined by Eq. (36), depends in some way on a scalar parameter λ. On identifying Eqs. (54) and (55) with Eq. (1), we obtain from the Hellmann–Feynman theorem (2):

$$\frac{\partial b_n^{\pm 1}(E)}{\partial\lambda} = \frac{(\Psi_n|(\partial\hat{\mathcal{B}}^{(\pm)}/\partial\lambda)\Psi_n)}{(\Psi_n|\beta^{(\pm)}\Psi_n)}, \tag{59}$$

$$\frac{\partial b_n^{\pm 1}(E)}{\partial\lambda} = \frac{(\Psi_n|(\partial\hat{\mathcal{R}}^{(\mp)}/\partial\lambda)\Psi_n)}{(\Psi_n|\beta^{(\mp)}\Psi_n)}. \tag{60}$$

Like Eqs. (19) and (20), relations (59) and (60) are formal and of no practical importance, since using in them the spectral expansions (57) and (58), respectively, we obtain only trivial identities.

To find more convenient expressions for $\partial b_n^{\pm 1}(E)/\partial\lambda$, we transform Eq. (53) to the form

$$b_n^{\pm 1}(E) = -\gamma^{(\mp)} \frac{(\Psi_n|\mathrm{i}\alpha_\perp^{(\pm)}\Psi_n)}{(\Psi_n|\beta^{(\pm)}\Psi_n)} \tag{61}$$

and differentiate the result with respect to λ, obtaining

$$\frac{\partial b_n^{\pm 1}(E)}{\partial\lambda} = -\gamma^{(\mp)} \frac{(\Psi_n|\mathrm{i}\alpha_\perp^{(\pm)}(\partial\Psi_n/\partial\lambda)) - \gamma^{(\pm)} b_n^{\pm 1}(E)(\Psi_n|\beta^{(\pm)}(\partial\Psi_n/\partial\lambda))}{(\Psi_n|\beta^{(\pm)}\Psi_n)}. \tag{62}$$

To proceed further, we employ identity (42) with

$$\Phi(\mathbf{r}) = \Psi_n(E,\mathbf{r}), \qquad \Phi'(\mathbf{r}) = \frac{\partial\Psi_n(E,\mathbf{r})}{\partial\lambda} \tag{63}$$

and, after making use of Eqs. (43) and (53), obtain

$$\gamma^{(\pm)} b_n^{\pm 1}(E)\left(\Psi_n\middle|\beta^{(\pm)}\frac{\partial\Psi_n}{\partial\lambda}\right) - \left(\Psi_n\middle|\mathrm{i}\alpha_\perp^{(\pm)}\frac{\partial\Psi_n}{\partial\lambda}\right) = \frac{1}{c\hbar}\left\langle\Psi_n\middle|[\hat{\mathcal{H}} - E]\frac{\partial\Psi_n}{\partial\lambda}\right\rangle, \tag{64}$$

which still may be transformed on utilizing

$$\left\langle\Psi_n\middle|[\hat{\mathcal{H}} - E]\frac{\partial\Psi_n}{\partial\lambda}\right\rangle = \left\langle\Psi_n\middle|\frac{\partial[\hat{\mathcal{H}} - E]\Psi_n}{\partial\lambda}\right\rangle - \left\langle\Psi_n\middle|\frac{\partial[\hat{\mathcal{H}} - E]}{\partial\lambda}\Psi_n\right\rangle \tag{65}$$

(notice that Eqs. (27) and (65) are only seemingly identical since the Hamiltonians used in them are defined differently). Since the first term on the right side of Eq. (65) vanishes identically, from Eqs. (64) and (65) we have

$$\left(\Psi_n\middle|\mathrm{i}\alpha_\perp^{(\pm)}\frac{\partial\Psi_n}{\partial\lambda}\right) - \gamma^{(\pm)} b_n^{\pm 1}(E)\left(\Psi_n\middle|\beta^{(\pm)}\frac{\partial\Psi_n}{\partial\lambda}\right) = \frac{1}{c\hbar}\left\langle\Psi_n\middle|\frac{\partial[\hat{\mathcal{H}} - E]}{\partial\lambda}\Psi_n\right\rangle. \tag{66}$$

On substituting this result to Eq. (62), we finally arrive at

$$\frac{\partial b_n^{\pm 1}(E)}{\partial\lambda} = -\frac{\gamma^{(\mp)}}{c\hbar}\frac{\langle\Psi_n|(\partial[\hat{\mathcal{H}} - E]/\partial\lambda)\Psi_n\rangle}{(\Psi_n|\beta^{(\pm)}\Psi_n)}. \tag{67}$$

Eq. (67) provides convenient analogs of the Hellmann–Feynman theorem in the relativistic R-matrix theory.

To illustrate the utility of result (67) we shall again consider the particular case $\lambda = E$. One then obtains

$$\frac{\partial b_n^{\pm 1}(E)}{\partial E} = \frac{\gamma^{(\mp)}}{c\hbar}\frac{\langle\Psi_n|\Psi_n\rangle}{(\Psi_n|\beta^{(\pm)}\Psi_n)}, \tag{68}$$

which implies (cf. Eq. (45)) that between their poles eigenvalues of $\hat{\mathcal{B}}^{(+)}(E)$ and $\hat{\mathcal{R}}^{(-)}(E)$ ($\hat{\mathcal{B}}^{(-)}(E)$ and $\hat{\mathcal{R}}^{(+)}(E)$) are monotonically *decreasing* (*increasing*) functions of energy.

In conclusion of this section, we owe the reader an explanation why the right side of Eq. (67) does not contain $A_\perp$-dependent surface terms similar to those appearing in the nonrelativistic formulas (29) and (31). The reason is that although the operators $\hat{\mathcal{B}}^{(\pm)}(E)$ and $\hat{\mathcal{R}}^{(\pm)}(E)$ introduced by us are *analogs* of the nonrelativistic operators $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{R}}(E)$, we have defined them so that in the nonrelativistic limit

$$\lim_{c\to\infty}\hat{\mathcal{B}}^{(+)}(E) \neq \hat{\mathcal{B}}(E), \qquad \lim_{c\to\infty}\hat{\mathcal{R}}^{(+)}(E) \neq \hat{\mathcal{R}}(E). \tag{69}$$

Eq. (69) does not violate any fundamental physical principles since none of the operators appearing in it is an observable. Rather, they are ‘intermediate’ objects, in terms of which observable quantities are expressed when the

R-matrix theory is applied to a specific problem. Therefore, one has a considerable degree of freedom in defining these operators. In our considerations we have used the criterion of simplicity, requiring $\hat{\mathcal{B}}(E)$ and $\hat{\mathcal{B}}^{(\pm)}(E)$ to be Hermitian and defined as simple as possible, and this has led us from Eqs. (6) and (42) to definitions (9) and (44). It is possible to redefine $\hat{\mathcal{B}}^{(+)}(E)$ and $\hat{\mathcal{R}}^{(+)}(E)$ (and, consequently, $\hat{\mathcal{B}}^{(-)}(E)$ and $\hat{\mathcal{R}}^{(-)}(E)$) so that Eq. (69) is replaced by

$$\lim_{c\to\infty} \hat{\mathcal{B}}^{(+)}(E) = \hat{\mathcal{B}}(E), \qquad \lim_{c\to\infty} \hat{\mathcal{R}}^{(+)}(E) = \hat{\mathcal{R}}(E), \tag{70}$$

but use of the operators satisfying conditions (70) appears to be more tedious than those obeying Eq. (69) and does not offer any actual advantages.

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