The application of generalized Wronskians to single-site scattering theory

1994 J. Phys. A: Math. Gen. 27 3787

(http://iopscience.iop.org/0305-4470/27/11/028)

J. Phys. A: Math. Gen. 27 (1994) 3787–3794. Printed in the UK

The application of generalized Wronskians to single-site scattering theory

S C Lovatt
H H Wills Physics Laboratory, University of Bristol, Tyndall Ave, Bristol, Avon, UK

Received 12 November 1993, in final form 17 March 1994

Abstract. The concept of the Wronskian determinant is generalized and shown to give rise to a projection operator which can be used in basis-function expansion schemes. This result is applied to relativistic single-site scattering theory and it is shown that formulae previously obtained on an *ad hoc* basis can be understood as special cases of a general Wronskian scattering identity. Finally, the form of the negative-energy scattering matrix is discussed.

1. Introduction

Wronskians play a central role in the formulae of scattering theory, e.g. [1, 2]. Two very different ways of viewing them can be distinguished. The first physical interpretation of the Wronskians encountered in scattering theory is that they are matrix elements of the (Schrödinger or Dirac) flux operators. However, this interpretation does not suggest *how* Wronskians will enter the formulae of scattering theory. Insight into this question can readily be gained from considering the second algebraic interpretation of the Wronskian.

Notation. The following notation has been adopted. Dirac four-component spinors are given a *tilde*, e.g. $\tilde{\Phi}$. Two-component spinors are given a *bar*, e.g. $\bar{\psi}$. Three-component real-space vectors are printed in heavy type and unit vectors given a *hat*, e.g. $\boldsymbol{W}(\hat{\boldsymbol{r}})$. Matrices are underlined whenever their indices are suppressed e.g. $\underline{\mathcal{T}}$.

2. Wronskian expansion

The Wronskian determinant of $\{f_n\}$, a set of N scalar functions of a single independent variable x, is defined as

$$W[\{f_n\}] = \begin{Vmatrix} f_1^{(0)} & f_2^{(0)} & f_3^{(0)} & \cdots & f_N^{(0)} \\ f_1^{(1)} & f_2^{(1)} & f_3^{(1)} & \cdots & f_N^{(1)} \\ f_1^{(2)} & f_2^{(2)} & f_3^{(2)} & \cdots & f_N^{(2)} \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ f_1^{(N)} & f_2^{(N)} & f_3^{(N)} & \cdots & f_N^{(N)} \end{Vmatrix} \tag{1}$$

where $f_n^{(m)} = (\mathrm{d}/\mathrm{d}x)^m f(x)$.

If the functions in this set are linearly independent up to their Nth derivative then their Wronskian is manifestly non-zero. Conversely it will be zero if any one or more of the

0305-4470/94/113787+08$19.50

functions involved can be expressed in terms of a linear combination of the others. It follows that if some function $g(x)$ is known to be exactly expressible as a finite sum of some $\{f_n\}$ (as will always be the case if it is a solution of some Nth-order differential equation), then

$$g(x) = \sum_{q=1}^{N} f_q(x) \left[\frac{W[g; \{f_{n\neq q}\}]}{W[\{f_n\}]} \right]_{x=x_0}$$

for *any* x_0 such that $W[\{f_n\}] \neq 0$ and where $W[g; \{f_{n\neq q}\}]$ signifies the Wronskian determinant where the place of the qth function (in the qth column) has been taken by the *target* function g which is to be expanded.

The form of this identity is intriguing. Generally, expansion formulae rely on orthogonality relationships involving *integration* over some range of an independent variable, whereas, here, only *differentials* evaluated at *a single value* of x appear. Moreover, the Wronskian formula can be applied whenever it is known that a target function can be expressed as a combination of *any* other functions and not just when these form a complete orthonormal set.

In fact, the Wronskian acts as a projection operator

$$\mathbf{P}_n g(x) = f_n(x) \left[\frac{W[g; \{f_{q\neq n}\}]}{W[\{f_q\}]} \right]_{x=x_0} \tag{3}$$

$$\mathbf{P}_m \mathbf{P}_n = \delta_{m,n} \mathbf{P}_n.$$

The concept of the Wronskian can be extended in a natural way to multicomponent functions of a single variable (such as the one-dimensional solution of the Dirac equation or the asymptotic form of a three-dimensional solution decomposed into angular-momentum channels). For such functions, however, the Wronskian is no longer uniquely defined. For example, it is possible to define a determinant for each and every component, and hybrid Wronskians which involve derivatives of various components of the basis functions can be defined. Moreover, the definition of *linear independence* has to be generalized; because functions that may be linearly independent as far as one component is concerned may not be when another is considered (for example a function could have some components that were identically zero).

Moreover, it can be useful to construct a hybrid Wronskian by replacing some or all of the rows of a single-component Wronskian with the value of other components (or lower derivatives thereof). This new Wronskian will still have the property of being non-zero only when the functions from which it is constructed are linearly independent, though now the exact specification that a set of functions must fulfil in order to qualify as *linearly independent* has changed. In the extreme case where N N-component functions form the expansion basis, the Wronskian can be written without any derivatives and equation (2) reduces to Kramer's rule for the solution of a set of linear simultaneous equations.

Because they must yield the same expansions for a given basis, all families of Wronskian determinants must be identical to within common normalization factors. However, for any family, certain values of the independent variable will make these normalization pre-factors *accidentally* zero and the corresponding projection operators take the form 0/0.

The marks of a good choice of Wronskian construction are that its zeros are remote from the range of the independent variable of interest and that it involves as few derivatives as possible. Moreover, to successfully expand a target function in a given basis, a convenient

set of criteria which unambiguously distinguish the basis functions from each other is required. It is this set of criteria that defines exactly what is meant by *linear independence*. Such a definition automatically follows whenever a 'boundary-matching problem' is set up in terms of the continuity properties of the target function. If such a problem can be formulated, it will certainly define a good Wronskian construction.

For solutions of the isotropic Dirac Hamiltonian, it is easy to show that the *non-relativistic* definition of the Wronskian

$$W[\tilde{\psi};\tilde{\phi}]^{\mathrm{nr}}_{r=r_0} = \left[\bar{\psi}_1 \frac{\mathrm{d}\bar{\phi}_1}{\mathrm{d}r} - \bar{\phi}_1 \frac{\mathrm{d}\bar{\psi}_1}{\mathrm{d}r}\right]_{r=r_0}$$

which involves radial derivatives of *one component* of the wavefunction *only*, is equivalent to the *relativistic* [3] or *two-component* definition

$$\begin{aligned} W[\tilde{\psi};\tilde{\phi}]^{\mathrm{rel}}_{r=r_0} &= [\bar{\psi}_1\bar{\phi}_2 - \bar{\psi}_2\bar{\phi}_1]_{r=r_0} \\ &= \mathrm{i}\tilde{\psi}^{\mathrm{T}}\underline{\sigma}_y\tilde{\phi} \end{aligned} \tag{4}$$

where $\tilde{\psi}^{\mathrm{T}}$ signifies the transpose (row) spinor.

3. The Wronskian scattering identity

The role of Wronskians in scattering theory can now be understood. In particular, the conventional technique of 'matching wavefunctions' or 'logarithmic derivatives' at the muffin-tin radius R_{MT} for a non-relativistic Hamiltonian with an isotropic finite-range potential

$$\frac{\hbar^2}{2m}\nabla^2 + V(r) \qquad V(r) = 0 \qquad r \geqslant R_{\mathrm{MT}} \tag{5}$$

(see, for example equation (5.25) in [4]), can easily be recognized as having the form of a Wronskian expansion quotient

$$\cot(\delta_\Lambda) = \mathrm{i}\frac{S_\Lambda + 1}{S_\Lambda - 1} = \frac{R'_\Lambda n_\ell - R_\Lambda n'_\ell}{R'_\Lambda j_\ell - R_\Lambda j'_\ell}$$

$$\begin{aligned} \mathbf{s}_\Lambda(\varepsilon) = \frac{\cot(\delta_\Lambda)+\mathrm{i}}{\cot(\delta_\Lambda)-\mathrm{i}} &= -\frac{R'_\Lambda(R_{\mathrm{MT}};\varepsilon)h^-_\ell(qR_{\mathrm{MT}}) - R_\Lambda(R_{\mathrm{MT}};\varepsilon)h^{-\prime}_\ell(qR_{\mathrm{MT}})}{R'_\Lambda(R_{\mathrm{MT}};\varepsilon)h^+_\ell(qR_{\mathrm{MT}}) - R_\Lambda(R_{\mathrm{MT}};\varepsilon)h^{+\prime}_\ell(qR_{\mathrm{MT}})} \\ &= +\frac{W[h^-_\ell;R_\Lambda]_{r\geqslant R_{\mathrm{MT}}}}{W[h^+_\ell;R_\Lambda]_{r\geqslant R_{\mathrm{MT}}}} \end{aligned} \tag{6}$$

where Λ signifies the quantum numbers κ and μ [5]; these are more commonly encountered in relativistic theory

$$\ell = J + \tfrac{1}{2}S_\kappa \qquad J = |\kappa| + \tfrac{1}{2} \qquad S_\kappa = \kappa/|\kappa| \qquad m_J = \mu \tag{7}$$

where δ_Λ is the scattering phase-shift associated with the angular-momentum channel with quantum numbers κ, μ; and j_ℓ, n_ℓ and $h^\pm_\ell$ are respectively the Bessel, Neumann and Hankel solutions of the spherical Bessel equation which constitute the free-space solutions of both

the Schrödinger and Dirac wave equations. The utility of the algebraic view of Wronskians presented here is that generalizations of formulae such as equation (6) can be written down immediately rather than derived at length from first principles. For example, the relativistic version of equation (6) can immediately be written down as

$$\cot(\delta_\Lambda) = +\frac{W[\tilde{h}_\Lambda^-; \tilde{R}_\Lambda]_{r\geqslant R_{MT}}}{W[\tilde{h}_\Lambda^+; \tilde{R}_\Lambda]_{r\geqslant R_{MT}}}.$$

The basic problem in scattering theory is that of characterizing the asymptotic behaviour of scattering solutions. This is equivalent to answering the question: 'How can the members of a complete set of time-independent solutions of a scattering Hamiltonian labelled in terms of their asymptotic incoming flux be expanded in terms of a second complete set of eigensolutions, specified in terms of their asymptotic outgoing flux?' In this approach, the scattering matrix **S** is viewed as the (unitary) transformation between the incoming and outgoing scattering solution bases.

The wavefunction beyond the range of the potential is fully specified by the problem's asymptotic boundary conditions. Moreover, it is not necessary to know the *complete* external solution in order to find the internal solution that matches it. Knowledge of either the asymptotic incoming *or* outgoing flux *alone* is sufficient. The required transformation between incoming and outgoing scattering solutions can be found by using a two-stage expansion procedure. First, a single incoming *free-space* wave $\tilde{h}_\Lambda^-$ is (incompletely) expanded beyond the range of the potential in terms of regular *internal* eigensolutions of the scattering Hamiltonian

$$\begin{aligned}\tilde{\Psi}_\Lambda(r) &= \sum_\nu c_{\Lambda,\nu}\tilde{\Phi}_\nu(r)\\ &= \tilde{h}_\Lambda^-(r) + \sum_{\Lambda'} \mathbf{S}_{\Lambda,\Lambda'}\tilde{h}_{\Lambda'}^+(r) \qquad r \geqslant R_{MT}\\ \tilde{h}_\Lambda^-(r) &= \sum_\nu c_{\Lambda,\nu}\tilde{\Phi}_\nu(r) + \text{a sum of } h_\Lambda^+\text{'s } \textit{only} \qquad r \geqslant R_{MT}\\ c_{\Lambda,\nu} &= \frac{W[\tilde{h}_\Lambda^-; \{\tilde{\Phi}_{\lambda\neq\nu}; \tilde{h}_\lambda^+\}]_{r\geqslant R_{MT}}}{W[\{\tilde{\Phi}_\lambda^-; \tilde{h}_\lambda^+\}]_{r\geqslant R_{MT}}} \qquad (8)\end{aligned}$$

where $\tilde{\Psi}_\Lambda^-$ is the full *internal* scattering solution with incoming asymptotic form $\tilde{h}_\Lambda^-$ and $\{\tilde{\Phi}_\lambda\}$ is the set of regular internal solutions. The Wronskian in the denominator of equation (8) is formed from all members of both specified sets. The notation used in its numerator signifies that the *targeted* incoming wave $\tilde{h}_\Lambda^-$ has been substituted for the νth regular solution. The irregular outgoing solutions are required when forming both numerator and denominator to ensure that the basis spans the target expansion function, $\tilde{h}_\Lambda^-$.

This full internal solution can be expanded (beyond the range of the potential) in terms of free-space spherical waves. It is then possible to understand formulae previously derived piecemeal for anisotropic scattering as special cases of the following general Wronskian scattering identity:

$$\begin{aligned}\tilde{\Psi}_\Lambda(r) &= \sum_{\Lambda',\pm} \frac{\pm\tilde{h}_{\Lambda'}^\pm(r)}{W[\{\tilde{h}_\lambda^+, \tilde{h}_\lambda^-\}]} W[\tilde{\Psi}_\Lambda; \{\tilde{h}_{\lambda\neq\Lambda'}^\pm, \tilde{h}_\lambda^\mp\}]\\ &= \sum_{\Lambda',\pm} \frac{\pm\tilde{h}_{\Lambda'}^\pm}{W[\{\tilde{h}_\lambda^+, \tilde{h}_\lambda^-\}]} W\left[\sum_\nu \tilde{\Phi}_\nu \frac{W[\tilde{h}_\Lambda^-; \{\tilde{\Phi}_{\lambda\neq\nu}, \tilde{h}_\lambda^+\}]}{W[\{\tilde{\Phi}_\lambda, \tilde{h}_\lambda^+\}]}; \{\tilde{h}_{\lambda\neq\Lambda'}^\pm, \tilde{h}_\lambda^\mp\}\right] \qquad (9)\end{aligned}$$

where all Wronskians are evaluated beyond R_{MT} but r is not so constrained. The **S**-matrix can be identified with the coefficient of $\tilde{h}^+_\Lambda$,

$$\mathbf{S}_{\Lambda',\Lambda} = \frac{\sum_\nu W[\tilde{\Phi}_\nu W[\tilde{h}^-_\Lambda; \{\tilde{\Phi}_{\lambda\neq\nu}, \tilde{h}^+_\lambda\}]; \{\tilde{h}^+_{\lambda\neq\Lambda'}, \tilde{h}^-_\lambda\}]}{W[\{\tilde{h}^+_\lambda, \tilde{h}^-_\lambda\}]W[\{\tilde{\Phi}_\lambda, \tilde{h}^+_\lambda\}]}. \tag{10}$$

Note that no reference has to be made to the form of the Hamiltonian at any stage of the discussion. This is typical of the scattering-matrix approach to physical processes. The analysis does presume that the wavefunctions are regular within the range of the potential.

4. Application to spin-polarized scattering

As an example of the application of equation (10), take the case of an isotropic electric scalar potential and a spherically-symmetric unidirectional *spin-only* magnetization, as studied by Strange *et al* [6] and later reviewed by Ebert and Gyorffy [3]. In this case, only two regular internal solutions of the Dirac equation, $\tilde{\Phi}^+$ and $\tilde{\Phi}^-$, need be considered because the magnetization can be assumed to couple together only channels with a common value of ℓ, the orbital angular momentum of their *large* or non-relativistic component [5, 6].

Asymptotically, both of these have components in only two angular-momentum channels $\Lambda^+ = (\kappa, \mu)$ and $\Lambda^- = (-[1+\kappa], \mu)$ whose angular functions are the *two by four* arrays [7] $\underline{\Xi}_{\Lambda^\pm}(\hat{r})$

$$\begin{aligned}
\lim_{r\to\infty} \tilde{\Phi}^-(r) &= \underline{\Xi}_{\Lambda^-}(\hat{r})\bar{\mathbf{R}}^-_{\Lambda^-}(r) + \underline{\Xi}_{\Lambda^+}(\hat{r})\bar{\mathbf{R}}^-_{\Lambda^+}(r) \\
\lim_{r\to\infty} \tilde{\Phi}^+(r) &= \underline{\Xi}_{\Lambda^-}(\hat{r})\bar{\mathbf{R}}^+_{\Lambda^-}(r) + \underline{\Xi}_{\Lambda^+}(\hat{r})\bar{\mathbf{R}}^+_{\Lambda^+}(r) \\
\underline{\Xi}^\mu_\kappa(\hat{r}) &= \begin{bmatrix} \bar{\mathcal{Y}}^\mu_\kappa(\hat{r}) & \bar{0} \\ \bar{0} & \mathrm{i}\bar{\mathcal{Y}}^\mu_{-\kappa}(\hat{r}) \end{bmatrix}.
\end{aligned} \tag{11}$$

$\bar{\mathcal{Y}}^\mu_\kappa(\hat{r})$ are the standard Dirac two-spinor angular-momentum functions.

The denominator in equation (8) becomes

$$W[\{\tilde{\Phi}_\lambda, \tilde{h}^+_\lambda\}] = \begin{Vmatrix} \bar{\mathbf{R}}^-_{\Lambda^-} & \bar{\mathbf{R}}^+_{\Lambda^-} & \bar{\mathbf{h}}^+_{\Lambda^-} & \bar{0} \\ \bar{\mathbf{R}}^-_{\Lambda^+} & \bar{\mathbf{R}}^+_{\Lambda^+} & \bar{0} & \bar{\mathbf{h}}^+_{\Lambda^+} \end{Vmatrix}$$

where the $\bar{\mathbf{R}}$s and $\bar{\mathbf{h}}^+$s are both two-component column arrays that are functions of r *only*. This determinant can be expanded as

$$W[\{\tilde{\Phi}_\lambda\}; \{\tilde{h}^+_\lambda\}] = W\left[\bar{\mathbf{R}}^+; \bar{\mathbf{h}}^+\right]_{\Lambda^-} W\left[\bar{\mathbf{R}}^-; \bar{\mathbf{h}}^+\right]_{\Lambda^+} - W\left[\bar{\mathbf{R}}^-; \bar{\mathbf{h}}^+\right]_{\Lambda^-} W\left[\bar{\mathbf{R}}^+; \bar{\mathbf{h}}^+\right]_{\Lambda^+}. \tag{12}$$

Each of these two-component Wronskians are evaluated asymptotically between pairs of radial functions belonging to the *same* angular-momentum channel as indicated by the suffix attached. The right-hand side of equation (12) is *minus* the denominator of the expression for the **S**-matrix given by Ebert and Gyorffy [3].

The inner Wronskian in the numerator of equation (10) reduces to terms such as

$$\begin{aligned}
W[\tilde{h}^-_{\Lambda 1}\{\Phi^+, \tilde{h}^+_\lambda\}] &= \begin{Vmatrix} \bar{\mathbf{h}}^-_{\Lambda^-} & \bar{\mathbf{R}}^+_{\Lambda^-} & \bar{\mathbf{h}}^+_{\Lambda^-} & \bar{0} \\ \bar{0} & \bar{\mathbf{R}}^+_{\Lambda^+} & \bar{0} & \bar{\mathbf{h}}^+_{\Lambda^+} \end{Vmatrix} \\
&= -W[\bar{\mathbf{h}}^-; \bar{\mathbf{h}}^+]_{\Lambda^-} W[\bar{\mathbf{R}}^+; \bar{\mathbf{h}}^+]_{\Lambda^+}
\end{aligned} \tag{13}$$

which in part cancel with the denominator to give the following formula for the **S**-matrix

$$\mathbf{s}_{\Lambda',\Lambda} = -\sigma \frac{W[\bar{\mathbf{R}}^{+};\bar{\mathbf{h}}^{-}]_{\Lambda'} W[\bar{\mathbf{R}}^{-};\bar{\mathbf{h}}^{+}]_{\bar{\Lambda}} - W[\bar{\mathbf{R}}^{-};\bar{\mathbf{h}}^{-}]_{\Lambda'} W[\bar{\mathbf{R}}^{+};\bar{\mathbf{h}}^{+}]_{\bar{\Lambda}}}{W[\bar{\mathbf{R}}^{+};\bar{\mathbf{h}}^{+}]_{\Lambda^+} W[\bar{\mathbf{R}}^{-};\bar{\mathbf{h}}^{+}]_{\Lambda^-} - W[\bar{\mathbf{R}}^{+};\bar{\mathbf{h}}^{+}]_{\Lambda^-} W[\bar{\mathbf{R}}^{-};\bar{\mathbf{h}}^{+}]_{\Lambda^+}} \tag{14}$$

where σ signifies either $+,-$; $\Lambda = \Lambda^{\sigma}$, $\bar{\Lambda} = \Lambda^{-\sigma}$ with equivalent relationships among the primed symbols.

This formula can be written in terms of Ebert's β and γ matrices

$$\mathbf{s}_{\Lambda',\Lambda} = -\sigma \frac{\alpha_{+,\sigma'}\beta_{-,\bar{\sigma}} - \alpha_{-,\sigma'}\beta_{+,\bar{\sigma}}}{\beta_{+,+}\beta_{-,-} - \beta_{+,-}\beta_{-,+}}$$

$$\alpha_{\sigma',\sigma} = W[\bar{\mathbf{R}}^{\sigma};\bar{\mathbf{h}}^{+}]_{\Lambda'}$$

$$\beta_{\sigma',\sigma} = W[\bar{\mathbf{R}}^{\sigma};\bar{\mathbf{h}}^{-}]_{\Lambda'}$$

$$\gamma_{\sigma',\sigma} = W[\bar{\mathbf{R}}^{\sigma};\bar{\jmath}]_{\Lambda'} = \tfrac{1}{2}(\alpha_{\sigma',\sigma} + \beta_{\sigma',\sigma}).$$

After further algebra

$$-2\mathrm{i}p\mathbf{t}_{\Lambda',\Lambda} = \mathbf{s}_{\Lambda',\Lambda} - \delta_{\Lambda',\Lambda} = \sigma'\sigma \frac{\gamma_{\sigma,\sigma'}\beta_{\bar{\sigma},\bar{\sigma}} - \gamma_{\sigma',\bar{\sigma}}\beta_{\bar{\sigma},\sigma}}{\beta_{+,+}\beta_{-,-} - \beta_{+,-}\beta_{-,+}}. \tag{15}$$

This formula is invariant on interchange of $R^{\pm}$, as it must be. It is entirely equivalent to those formulae given in [3] except for a manifestly erroneous index in one of them.

5. The scattering matrix for negative energies

It is common knowledge that the positive-energy **S**-matrix is unitary and a simple proof of this using Wronskian manipulations is given in appendix A of [8]. The argument rehearsed there to reach the conclusion $\mathbf{s}^{\dagger} = \mathbf{s}^{-1}$ (equation (A4) of [8]) does not carry over to negative energies as it assumes the identity

$$\bar{\mathbf{h}}_{\kappa}^{\pm *}(z) = \bar{\mathbf{h}}_{\kappa}^{\mp}(z)$$

which is only true for real $z = kr$ (where k is radial momentum) and, hence, positive energy. For negative energies, $z = q + \mathrm{i}\mu$ (q and μ both real) becomes purely imaginary and the Hermitian conjugate of $\bar{\mathbf{h}}_{\kappa}^{\pm}$ becomes

$$\bar{\mathbf{h}}_{\kappa}^{\pm\dagger}(\mathrm{i}\mu) = \frac{q}{(2R)^{1/2}} \frac{1}{(2\varepsilon)^{1/2}} [(\varepsilon + m_e c^2)^{1/2}(-1)^{\ell} h_{\ell}^{\pm}(\mathrm{i}\mu), -S_{\kappa}(\varepsilon - m_e c^2)^{1/2}(-1)^{\bar{\ell}} h_{\bar{\ell}}^{\pm}(\mathrm{i}\mu)]$$

where

$$\bar{\ell}(\kappa) = \ell(-\kappa) = \ell(\kappa) - S_{\kappa}.$$

The additional minus sign before the S_{κ} comes from the fact that $(\varepsilon - m_e c^2)^{1/2}$ is imaginary.

$$\begin{aligned}\bar{\mathbf{h}}_{\kappa}^{\pm\dagger}(\mathrm{i}\mu) &= \frac{q}{(2R)^{1/2}} \frac{1}{(2\varepsilon)^{1/2}} (-1)^{\ell} [(\varepsilon + m_e c^2)^{1/2} h_{\ell}^{\pm}(\mathrm{i}\mu), +S_{\kappa}(\varepsilon - m_e c^2)^{1/2} h_{\bar{\ell}}^{\pm}(\mathrm{i}\mu)] \\ &= (-1)^{\ell} \bar{\mathbf{h}}_{\kappa}^{\pm T}(\mathrm{i}\mu)\end{aligned} \tag{16}$$

where $\bar{\mathbf{h}}_\kappa^{\pm T}$ is the *two by one* row array with elements identical to those of the *one by two* column array $\bar{\mathbf{h}}_\kappa^{\pm}$.

The following holds for any two linearly independent internal solutions labelled by Q_1 and Q_2:

$$W[\tilde{\Phi}_{Q_1}; \tilde{\Phi}_{Q_2}] = 0$$

$$\sum_\Lambda [\mathbf{a}^*_{\Lambda,Q_1}(-1)^\ell \bar{\mathbf{h}}^{+T}_\Lambda + \mathbf{b}^*_{\Lambda,Q_1}(-1)^\ell \bar{\mathbf{h}}^{-T}_\Lambda] \underline{\sigma}_y [\mathbf{a}_{\Lambda,Q_2} \bar{\mathbf{h}}^{+}_{\Lambda'} + \mathbf{b}_{\Lambda,Q_2} \bar{\mathbf{h}}^{-}_{\Lambda'}] = 0. \quad (17)$$

Using the fact that the Wronskians in equation (17) are independent of r (see equation (13) in [8])

$$\underline{\mathbf{a}}^\dagger \underline{\mathbf{m}} \underline{\mathbf{b}} = \underline{\mathbf{b}}^\dagger \underline{\mathbf{m}} \underline{\mathbf{a}}$$

where $\underline{\mathbf{m}}$ is diagonal with elements $\delta_{\Lambda',\Lambda}(-1)^\ell$, so

$$(\underline{\mathbf{m}} \underline{\mathbf{a}} \underline{\mathbf{b}}^{-1})^\dagger = \underline{\mathbf{m}} \underline{\mathbf{a}} \underline{\mathbf{b}}^{-1}$$

$$\underline{\mathbf{s}}^\dagger = \underline{\mathbf{m}} \underline{\mathbf{s}} \underline{\mathbf{m}}. \quad (18)$$

The matrix $\underline{\mathbf{m}} \underline{\mathbf{s}}$ is therefore Hermitian with *real* eigenvalues for negative energies. Moreover, if $\{u_j\}$ are the eigenvectors of $\underline{\mathbf{s}}$ with eigenvalues s_j then the following relationship is easily obtained:

$$(s_i^* - s_j) u_i^\dagger \underline{\mathbf{m}} u_j = 0. \quad (19)$$

This means that either two eigenvectors of the **s**-matrix are *orthogonal* in the sense that $u_i^\dagger \underline{\mathbf{m}} u_j = 0$ or that they must have eigenvalues which are complex conjugates of each other. Clearly, a normalized eigenvector will not generally be *self-orthogonal*, as the sum of the moduli of its components is unity and the effect of $\underline{\mathbf{m}}$ is just to negate half of the terms in this sum

$$u_j^\dagger u_j = \sum_\Lambda |u_{\Lambda,j}|^2 = 1 \qquad u_j^\dagger \underline{\mathbf{m}} u_j = \sum_\Lambda (-1)^\ell |u_{\Lambda,j}|^2. \quad (20)$$

Generally speaking, the eigenvalues of the negative-energy **s**-matrix must therefore be real. Moreover, if each eigenvector is considered as a function of energy, it is apparent that no eigenvalue of $\underline{\mathbf{s}}$ can ever be complex unless its eigenvector is *self-orthogonal* over an *extended range* of energies.

The negative-energy **s**-matrix can be decomposed into two interpenetrating matrices. The first consists of the leading diagonal and those off-diagonal elements that couple angular-momentum channels which differ in ℓ by an *even* integer. This matrix is *Hermitian*. The second *anti-Hermitian* matrix consists of those off-diagonal elements that couple channels differing in ℓ by an *odd* integer. The relativistic κ', κ block structure of the **s**-matrix for negative energies can be represented for $|\kappa| \leqslant 3$ as

$$\begin{bmatrix}
 & -1 & +1 & -2 & +2 & -3 & +3 \\
-1 & S_{-1,-1} & S_{-1,+1} & S_{-1,-2} & S_{-1,+2} & S_{-1,-3} & S_{-1,+3} \\
+1 & -S^\dagger_{-1,+1} & S_{+1,+1} & S_{+1,-2} & S_{+1,+2} & S_{+1,-3} & S_{+1,+3} \\
-2 & -S^\dagger_{-1,-2} & +S^\dagger_{+1,-2} & S_{-2,-2} & S_{-2,+2} & S_{-2,-3} & S_{-2,+3} \\
+2 & +S^\dagger_{-1,+2} & -S^\dagger_{+1,+2} & -S^\dagger_{-2,+2} & S_{+2,+2} & S_{+2,-3} & S_{+2,+3} \\
-3 & +S^\dagger_{-1,-3} & -S^\dagger_{+1,-3} & -S^\dagger_{-2,-3} & +S^\dagger_{+2,-3} & S_{-3,-3} & S_{-3,+3} \\
+3 & -S^\dagger_{-1,+3} & +S^\dagger_{+1,+3} & +S^\dagger_{-2,+3} & -S^\dagger_{+2,+3} & -S^\dagger_{-3,+3} & S_{+3,+3}
\end{bmatrix}$$

where each sub-matrix on the diagonal is Hermitian.

6. Conclusions

The application of Wronskians to basis-function expansion has been discussed. A general Wronskian scattering identity has been derived and shown to give rise naturally to a number of results in single-site scattering theory.

Acknowledgments

I would like to thank P Miller, B L Gyorffy and J N Sackett for helpful discussions; and J B Pendry and R Evans for encouragement to publish this work which was partly financed by SERC award 90101004.

References

[1] Tamura E 1992 *Phys. Rev.* B **45** 3271
[2] Butler W H, Zhang X-G and Gonis A 1992 *Mater. Res. Soc. Symp. Proc.* **253** 205
[3] Ebert H and Gyorffy B L 1991 *J. Phys. F: Met. Phys.* **18** 451
[4] Weinberger P 1990 *Electron Scattering Theory for Ordered and Disordered Matter* (Oxford: Clarendon)
[5] Rose M E 1961 *Relativistic Electron Theory* (New York: Wiley)
[6] Strange P, Staunton J B and Gyorffy B L 1984 *J. Phys. C: Solid State Phys.* **17** 3355
[7] Lovatt S C 1993 Relativistic single-site scattering theory for space-filling potentials *PhD Thesis* Bristol University
[8] Lovatt S C, Gyorffy B L and Guo G Y 1993 *J. Phys.: Condens. Matter* **5** 8005