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A unified review of Bloch operator modified Kohn variational methods

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A unified review of various Kohn variational methods for scattering calculations is presented using appropriate Bloch operators. Previous expressions are generalized slightly to use either an infinite range or a finite range of the scattering coordinate, or to use a basis set with non-fixed log derivative boundary conditions. A non-variational method (method of moments) is used in the derivations; the results are confirmed by Kohn variational derivations. Speculative linear variation functionals are introduced to connect both derivations. A model calculation of K (reactance) matrix is presented using a finite range and real algebra which is free of the so called 'Kohn anomaly', unlike the conventional Kohn method for the K matrix.

1. Introduction

Among the various basis set methods obtained from applications of the variational principles, those obtained by the Kohn variational principle [1] which is based on the Schrödinger equation (SE) has a distinct advantage over methods using other variational principles, e.g., Schwinger's (SVP) which is based on the Lippmann–Schwinger equation [2]. It is the 'simplicity' of the Kohn variation functional which enables the straightforward calculation of the matrix elements involved and a straightforward extension to complicated problems.

Other methods like those based on the Lippmann–Schwinger equation involve the reference Green's operator. This makes the matrix element calculations more complicated since a double integral is involved because the Green's operator is an integral operator. In addition, the integrals must often be recalculated at each scattering energy because the reference Green's operator is energy dependent. (The latter difficulty may be avoided when the SVP method is used to calculate the log derivative (Y) matrix using a fixed reference energy Green's operator in a finite range calculation [3].)

By contrast, the Kohn variational methods involve only single (not double) integration in the scattering coordinate and most of the integrals can be made energy independent. These features are quite important in multichannel reactive scattering calculations for many energies. Of course, other methods like the SVP have their own advantages, such as relatively fast convergence with respect to the basis set size [4], since the reference Green's operator, by taking care of the zero-order dynamics, reduces the 'work' which has to be done by the basis set. A more detailed discussion of Kohn variational methods in relation with other variational methods was given by Miller [5], for example.

The only serious difficulty with the Kohn variational methods was the spurious singularity (the so called 'Kohn anomaly') which occurred in calculating the K matrix (reactance matrix). This really was caused by a faulty application of the method [6].

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However, once the origin of this anomaly (i.e., the basis set linear dependence) was understood [6–8], many ways of avoiding this problem were devised. These include using partly complex basis functions and calculating the S matrix [9] or using linearly independent real basis functions and calculating the Y matrix [10], rather than the K matrix. Indeed, as a byproduct of the work below we derive another approach for the calculation of the K matrix using a finite range and linearly independent real basis functions which does not suffer from the spurious singularity.

In this paper, we show that systematic modifications of the previous Kohn variational methods by appropriate Bloch operators [11] allow us to use a wide class of basis sets which may remove some undesirable features of the previous Kohn methods. This quite simple and unified approach yields the variational expressions for all the scattering matrices: the S, K, T, Y, and R matrices of conventional scattering theory.

For the S, K, and T matrix calculations, the present expressions are valid for general ranges of the wavefunctions (or, equivalently, the integration ranges of the matrix elements). The range could be infinite as in the conventional versions [6, 9] or finite. These 'general range' expressions reduce to the conventional infinite range versions when the basis set and the range are those of the conventional methods. In this latter case, the inclusion of the Bloch operator has no effect at all on the computation. However, if we use a basis defined only in a finite range and, consequently, use the same finite range for integrations, the Bloch operator plays the role of imposing the correct asymptotic boundary conditions.

For the R and Y matrix calculations, the present approach makes it possible to use an inhomogeneous basis set (or, equivalently, a basis in which the log derivatives at the boundary do not have a fixed value). The use of inhomogenous basis functions conveniently circumvents the notorious 'slow convergence' problem in conventional R matrix theory in which the basis set used was homogeneous (or, equivalently, of fixed log derivative at the outer boundary). Such a basis is an improper basis to represent arbitrary functions at the boundary. Similarly, if we use a conventional homogeneous basis set, the resulting expression reduces to the conventional (slowly convergent) one, because the effect of operating with the Bloch operator on the basis functions is identically zero [12, 13]. However, as stated above, it has been demonstrated [6] that the use of inhomogeneous basis sets gives more rapid convergence to accurate results. This can be implemented quite simply by introducing the Bloch operator. A definite advantage of R matrix theory lies in the property that most (or even all) of the integrals can be made energy independent, which is important in calculations for many energies. This finite range version is in the same spirit as conventional R matrix theory in which the configuration space is divided into the internal region corresponding to our finite range and the external region where we assume the solutions are already known.

Manolopoulos and Wyatt introduced a particular type of inhomogeneous basis set (Lobatto shape functions), $\{u_i; u_1(0) = 0, u_0(a) = 1, u_{i\neq 0}(a) = 0\}$ defined on $[0, a]$, satisfying the so called $(0, 1)$ boundary conditions in their calculation of the log derivative matrix, Y. They used it successfully for realistic applications [10]. We also note that a different generalization of the Kohn variational principle exclusively for a finite range case was suggested recently by Brown and Light [14].

In short, the proper inclusion of the Bloch operator into the conventional Kohn variational methods make them generalized and/or more favourable in accuracy by removing some restrictions on the basis set.

We begin with some preliminary definitions in section 2. In section 3, we derive the generalized Kohn variational methods using the method of moments [4] which is simpler to apply than the conventional Kohn variational principle. Of course, it produces identical final expressions as does the application of the variational principle. We confirm that the final generalized Kohn variational methods are variationally stable by direct applications of the modified Kohn variational principles in section 4. One speculative reason behind this equivalence between the two derivations is given through the introduction of novel Kohn variation functionals which are linear in the unknown trial functions rather than bilinear as are conventional functionals in section 5. In any case the alternative derivation of the variational results is interesting. We present a brief conclusion and discussion in section 6.

2. Preliminaries

For simplicity of presentation, we restrict our notation to a one-dimensional s wave radial scattering case. The extension to more complicated problems is straightforward (at least formally). We use atomic units ($\hbar = 1$) in this paper. Before presenting the main theory, we need several definitions to simplify the following procedures.

The usual definition of the bra-ket is changed to omit the complex conjugation of the bra function [9, 15]:

$$\langle f|g\rangle = \int fg\,dr,$$

which also corresponds to the closure relation of biorthogonal basis functions of a complex symmetric matrix representation of a non-Hermitian Hamiltonian operator in complex scaling theory [15]. We note that a similar definition was used in Miller and coworkers' derivation of the Kohn variational S matrix approach [9]. We use a left handed arrow with an operator to indicate the function on the left is operated on by the operator, such as

$$\langle f|\overleftarrow{A}|g\rangle = \langle g|A|f\rangle.$$

The Bloch operator L was introduced some time ago by Bloch [11] to make the modified Hamiltonian operator, $H+L$, Hermitian on a finite range of the scattering coordinates, independent of the basis. The Bloch operator operates to nullify the 'non-Hermitian' surface terms introduced by considering only a finite scattering range. Thus the standard Bloch operator L is defined to cancel surface derivative terms at the boundary of the coordinate range of interest.

It is useful to point out explicitly the symmetry property of matrix elements of the Hamiltonian when modified with the Bloch operator. For f, g regular at the origin it yields the manifestly symmetric form:

$$\langle f|H+L-E|g\rangle = \langle g|H+L-E|f\rangle = \int_0^a \left\{\frac{1}{2m}f'g' + f(V-E)\,g\right\}dr - bf(a)\,g(a),$$

where V is the potential, m is the mass, E is the energy, the integration range is $[0, a]$, and the Bloch operator L is defined with a Dirac delta function as

$$L = L(b) = \frac{1}{2m}\delta(r-a)\left(\frac{d}{dr} - b\right). \tag{1}$$

It should also be understood that the integration range includes the infinitely small range of the delta function. The wavefunctions are scaled by $(1/r)$ in a standard way so that the Hamiltonian operator is defined with the volume element of $d\tau = \sin\theta\, \mathrm{d}r\, \mathrm{d}\theta\, \mathrm{d}\phi$ where θ and ϕ are the polar angles. Thus the matrix representation of $H+L-E$ is symmetric independent of the characteristics of the basis functions (whether vanishing at the outer boundary or not; of course they are regular functions, thus they vanish at the origin or the inner boundary). Note that we will use different values of 'b' for various matrices of scattering quantities below.

The S, K, and T scattering matrices are defined by the asymptotic functional forms we use for the asymptotic wave function. They are given by

$$\psi \to I - O\mathbf{S},$$
$$\psi \to S + C\mathbf{K},$$
$$\psi \to S + O\mathbf{T},$$

where I is the incoming wave, O the outgoing wave, and S and C the sine and cosine functions asymptotically. These expressions are valid in the asymptotic region(s), and are defined explicitly below. The Y and R matrices, on the other hand, are defined as log derivative (Y) and inverse log derivative (R) matrices at a *surface* normal to the scattering coordinate. In the asymptotic region they may be converted simply to any of the scattering matrices above. In the section below we derive equations for each of these matrices using the appropriate Bloch operators.

3. Derivations via method of moments

First we will present the generalized stationary expression for the S matrix valid for a general range using the method of moments [4]. Then we will present briefly the expressions for other scattering quantities.

3.1. *S matrix*

The I and O functions are defined as the incoming and outgoing waves, perhaps regularized by a proper cutoff function $f(r)$ such that, for large r,

$$I = f(r)\left(\frac{m}{k}\right)^{1/2} \exp(-ikr) \to \left(\frac{m}{k}\right)^{1/2} \exp(-ikr),$$

and

$$I(0) = 0,$$

where m and k are the system reduced mass and wavenumber, respectively. The cutoff function $f(r)$ is zero at the origin (or inner boundary), monotonic, and reaches unity before the outer boundary of the basis set range. O is simply the complex conjugate of I. (We apologize to readers for using I for a quantity other than the unit matrix.)

The wavefunction ψ satisfying the outgoing S matrix asymptotic boundary conditions can be expanded in a finite basis set $\{I, \phi_i\}$ as

$$\psi = I + \chi \to I - O\mathbf{S}, \tag{2}$$

$$\chi = c_0\, \phi_0 + \sum_{i \neq 0} c_i \phi_i, \tag{3}$$

where $\mathbf{S}$ is the S matrix and ϕ_0 is either an arbitrary 'boundary' function satisfying

$\phi_0(a) \neq 0$ when the range is finite $[0, a]$ or an outgoing wave O when the range is infinite. The functions $\phi_{i \neq 0}$ are localized ($\mathscr{L}^2$) type and may be real. We assume that all the basis functions are properly regularized so that ψ is the regular solution of the SE. We also assume that the asymptotic behaviour is achieved before the outer boundary a in the finite range case.

The trial function χ or, equivalently, the expansion coefficients $\{c_i\}$ of equation (3) should be determined so that the ψ is a good approximate solution of the SE. Defining the Bloch operator such that $L\chi = 0$ (see below), we may write the SE with the Bloch operator as

$$(H-E)\,\psi = (H-E)\,I + (H-E)\,\chi = (H-E)\,I + (H+L-E)\,\chi = 0, \tag{4}$$

where the non-trivial function χ can be determined by inverting the matrix representation of $H+L-E$ in the basis $\{\phi_i\}$:

$$\chi = -(H+L-E)^{-1}(H-E)\,I. \tag{5}$$

To ensure that $L\chi = 0$, we use the property that $\chi = -O\mathbf{S}$ at $r = a$ so that

$$L\chi = \frac{1}{2m}\delta(r-a)\left(\frac{\mathrm{d}}{\mathrm{d}r} - ik\right)\chi = \frac{1}{2m}\delta(r-a)\left(\frac{\mathrm{d}}{\mathrm{d}r} - ik\right)(-O\mathbf{S}) = 0. \tag{6}$$

Thus the Bloch operator L must be defined with $b = ik$, and we note that this Bloch operator is energy dependent and effective only at a. Incidentally, we see that the operation of L has null effect if the 'boundary' basis function ϕ_0 is the outgoing wave O and the integrations are done for an *infinite* range [9]. For other cases, the L will impose the correct boundary conditions at the (outer) boundary using the proper basis $\{\phi_i\}$.

Equation (5) amounts to the result of an application of the method of moments since it is equivalent to the result of projecting equation (4) onto ϕ_i basis functions. Also note that L ensures the symmetry of the matrix representation of $H+L-E$ for any proper basis set which is closely related with the stationary property of the final expression for the S matrix (section 4).

The final projection of the SE (equation (4)) onto the last remaining basis function, i.e., I, gives the expression for $\mathbf{S}$, after using integration by parts twice, as

$$\langle I|H-E|\,\psi\rangle = \langle\psi|H-E|\,I\rangle + i\mathbf{S} = 0, \tag{7}$$

where the integration range encompasses the interaction region so that the upper limit lies in the asymptotic region where ψ behaves as in equation (2). Use of equations (2), (5) and (7) leads to

$$\begin{aligned} -i\mathbf{S} &= \langle\psi|H-E|\,I\rangle = \langle I|\overleftarrow{H}-E|\,\psi\rangle \\ &= \langle I|H-E|\,I\rangle - \langle I|(\overleftarrow{H}-E)(H+L-E)^{-1}(H-E)|\,I\rangle. \end{aligned} \tag{8}$$

In short, one obtains the general range S matrix expression of equation (8) by requiring that the projection of the SE onto every basis function of ψ be zero, i.e., that ψ be a solution such that

$$\langle I|H-E|\,\psi\rangle = 0, \text{ and } \langle\phi_i|H-E|\,\psi\rangle = 0 \quad \text{for } i \geqslant 0.$$

Equation (8) is valid for general range with its corresponding proper basis set. In particular, for a finite range, ϕ_0 need not be (but of course, can be) O; any arbitrary

'boundary' function ($\phi_0(a) \neq 0$) which may be real and energy-independent can also serve as a basis function. However, there is no obvious advantage in doing so since the matrix elements involving O can be obtained simply as the complex conjugates of those involving I, which have to be evaluated anyway.

3.2. *K matrix*

On the other hand, in the K matrix calculation the use of a finite range and an arbitrary boundary function has a definite advantage over the infinite range version (or the case in which ϕ_0 is real and energy dependent), i.e., the 'Kohn anomaly' is automatically avoided. The K matrix equation is obtained similarly to the above by using the appropriate asymptotic boundary conditions and an appropriate Bloch operator.

The asymptotic behaviour of ψ is

$$\psi \to S + C\mathbf{K},$$

where $\mathbf{K}$ is the K matrix and S, C are the regularized sine-like and cosine-like functions, respectively, satisfying the boundary conditions as

$$S = f(r)\left(\frac{m}{k}\right)^{1/2} \sin kr \to \left(\frac{m}{k}\right)^{1/2} \sin kr, \qquad S(0) = 0,$$

$$C = f(r)\left(\frac{m}{k}\right)^{1/2} \cos kr \to \left(\frac{m}{k}\right)^{1/2} \cos kr, \qquad C(0) = 0,$$

Following equations parallel to equations (3–8), we find the K matrix expression as

$$\frac{\mathbf{K}}{2} = \langle S|H-E|S\rangle - \langle S|(\overleftarrow{H}-E)(H+L-E)^{-1}(H-E)|S\rangle, \tag{9}$$

where the Bloch operator for the K matrix calculation is defined as

$$L = L(-k\tan kr) = \frac{1}{2m}\delta(r-a)\left(\frac{\mathrm{d}}{\mathrm{d}r} + k\tan kr\right).$$

And we see that, as desired,

$$L(-k\tan kr)\,C = 0,$$

which plays the role of imposing the K matrix boundary conditions.

It was pointed out that the Kohn anomaly in the K matrix calculation occurs when the cosine-like function vanishes at the effective boundary a of the $\mathscr{L}^2$ functions and consequently becomes effectively linearly dependent at certain energies on the other $\mathscr{L}^2$ functions (which vanish at a) [6, 8]. This results in singular behaviour of the full Green's operator representation.

It is important to recognize that real representations of the Green's operator using *linearly independent* real basis functions do not generally show the Kohn anomaly in practical applications. Because the scattering energy interval of numerical instability around the real pole of the representation is extremely small (governed by computer accuracy), it is unlike that of the usual Kohn anomaly, which is caused by the use of

energy dependent real basis functions. At the energies of the Kohn anomalies these become linearly dependent on the fixed basis, and this results in a large energy interval of numerical instability. Thus, to avoid the usual Kohn anomaly we may choose the arbitrary function ϕ_0 (equation (3)) to be linearly independent of the other $\mathscr{L}^2$ basis functions at any energy. It is also convenient to use an energy independent real ϕ_0 to save computation of energy dependent integrals.

In figure 1, for a model van der Waals molecule, we compare the phase shift calculations which use the cosine-like function with those using an energy independent function for ϕ_0 (using real algebra). It is obvious that a 'Kohn anomaly' in the former case disappears in the latter case.

3.3. *T matrix*

With the T matrix boundary conditions given as

$$\psi \to S + O\mathbf{T},$$

where the S and O functions are defined above, we use the Bloch operator to obtain the generalized expression for the T matrix ($\mathbf{T}$) as

$$-\frac{\mathbf{T}}{2} = \langle S|H-E|S\rangle - \langle S|(\overleftarrow{H}-E)(H+L-E)^{-1}(H-E)|S\rangle, \tag{10}$$

where the Bloch operator is the same as that in the S matrix expression (equation (6)) which imposes the proper boundary conditions.

3.4. *Log derivative* (Y) *matrix*

The log derivative matrix $\mathbf{Y}$ is defined at an asymptotic position a where it is $\psi'(a)/\psi(a)$ in our one-dimensional case. Manolopoulos and Wyatt [10] introduced the $(0, 1)$ basis set defined on $[0, a]$:

$$\{u_i; u_i(0) = 0, u_0(a) = 1, u_{i\neq 0}(a) = 0\}.$$

This basis set is convenient in deriving the stationary expression for the Y matrix using the Kohn variational principle because only one function, u_0, is nonzero at a. We can arrive at the same expression using the method of moments as follows.

The wavefunction ψ is expanded as

$$\psi = u_0 + \chi = u_0 + \sum_{i\neq 0} c_i u_i,$$

where

$$\psi(a) = u_0(a) = 1,$$

then the SE for ψ is

$$(H-E)\,\psi = (H-E)\,u_0 + (H-E)\,\chi = 0,$$

and the log derivative matrix becomes simply

$$\mathbf{Y} = \frac{\psi'(a)}{\psi(a)} = \psi'(a).$$

The Green's operator $(H-E)^{-1}$ is represented by the 'interior' basis $\{u_{i\neq 0}\}$ only and

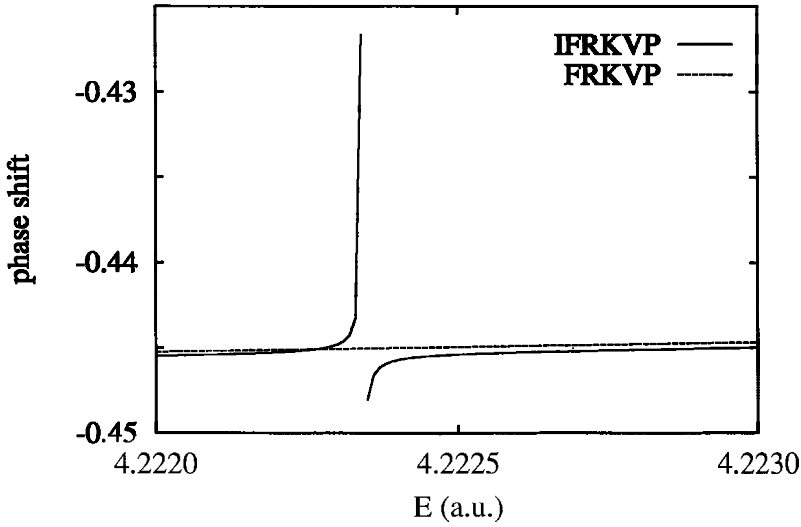

Figure 1. Phase shifts calculated by K matrix using an energy dependent cosine-like function (IFRKVP) and an energy independent S shape boundary function (FRKVP). At E = 4.22234, the cosine-like function vanishes at the outer boundary, leading to a 'linear dependence' anomaly. The calculation is for s wave radial scattering of a model spherical van der Waals molecule.

we define $L = L(0)$ (equation (1)). By using the fact that $\langle u_i|L|u_j\rangle = 0$ for any u_j functions if u_i is not the 'boundary' function u_0, we apply the method of moments to obtain

$$\chi = -(H-E)^{-1}(H-E)\,u_0 = -(H+L-E)^{-1}(H+L-E)\,u_0.$$

The final projection of the SE onto u_0 gives

$$\langle u_0|H-E|\,\psi\rangle = \langle u_0|H+L-E|\,\psi\rangle - \langle u_0|L|\psi\rangle = 0,$$

or

$$\begin{aligned}\frac{1}{2m}\mathbf{Y} = \langle u_0|L|\,\psi\rangle &= \langle u_0|H+L-E|\,\psi\rangle \\ &= \langle u_0|H+L-E|\,u_0\rangle \\ &\quad - \langle u_0|(H+L-E)(H+L-E)^{-1}(H+L-E)|\,u_0\rangle, \qquad (11)\end{aligned}$$

where we used

$$\langle u_0|L|\,\psi\rangle = \frac{1}{2m}u_0(a)\,\psi'(a) = \frac{1}{2m}\psi'(a) = \frac{1}{2m}\mathbf{Y},$$

which was derived variationally by Manolopoulos and Wyatt [10].

3.5. *R matrix*

The R matrix $\psi(a)/[\psi'(a)-b\psi(a)]$, which is identical to the inverse of the Y matrix in a particular case ($b = 0$), can be derived also using an appropriate Bloch operator (formally any b is appropriate in this case). Here any basis set $\{\phi_i;\ \phi_i(a) \neq 0$ for at least one $i\}$ can be used to expand the wavefunction [13].

Rearranging the SE gives

$$(H-E)\,\psi = (H+L-E)\,\psi - L\psi = 0,$$

from which we obtain

$$\psi = (H+L-E)^{-1}\,L\psi. \tag{12}$$

The R matrix (**R**) can be extracted as

$$\langle\psi|\overleftarrow{L}|\,\psi\rangle = \frac{1}{2m}\{\psi'(a)-b\psi(a)\}\,\psi(a)$$

$$= \frac{1}{2m}\{\psi'(a)-b\psi(a)\}^2\frac{\psi(a)}{\psi'(a)-b\psi(a)} = \frac{1}{2m}\{\psi'(a)-b\psi(a)\}^2\,\mathbf{R}. \tag{13}$$

Using the expression for ψ from equation (12) for the ket ψ in equation (13), we obtain

$$\frac{1}{2m}\{\psi'(a)-b\psi(a)\}^2\,\mathbf{R} = \langle\psi|\overleftarrow{L}(H+L-E)^{-1}\,L|\,\psi\rangle$$

$$= \left(\frac{1}{2m}\right)^2\{\psi'(a)-b\psi(a)\}\,\langle a|(H+L-E)^{-1}|\,a\rangle\,\{\psi'(a)-b\psi(a)\},$$

or

$$2m\mathbf{R} = \langle a|(H+L-E)^{-1}|\,a\rangle, \tag{14}$$

where the ket of a denotes the position eigenvector corresponding to a. Note that the actual values of $\psi(a)$ or $\psi'(a)$ were cancelled in the final expressions, and thus never need to be calculated.

We note that Meyer [16] recently used the same non-variational procedure to show the equivalence of the S matrix calculated via the Y matrix or the R matrix (with $b = 0$) *if* the $(0, 1)$ basis set of Manolopoulos and Wyatt is used.

Both the Y and R matrices can be converted to the S matrix or other scattering information by combining them with appropriate asymptotic boundary conditions at the surface a, in obvious ways. For example, the S matrix can be obtained from the Y matrix as

$$\mathbf{Y} = \frac{\psi'(a)}{\psi(a)} = \frac{I'(a)-O'(a)\,\mathbf{S}}{I(a)-O(a)\,\mathbf{S}},$$

or

$$\mathbf{S} = \frac{\mathbf{Y}I(a)-I'(a)}{\mathbf{Y}O(a)-O'(a)}.$$

Similar expressions can be derived in terms of the R matrix.

3.6. *S matrix via R matrix theory*

Direct evaluation of, for example, the S matrix is possible in the context of R matrix theory without the intermediate calculation of the Y or R matrix if we use the Bloch operator with $b = ik$ so that $LO = 0$. Then equation (12) can be rewritten, since ψ satisfies the S matrix asymptotic boundary conditions, as

$$\psi = (H+L-E)^{-1}\,L(I-O\mathbf{S}) = (H+L-E)^{-1}\,LI, \tag{15}$$

where we used the fact that L is an operator multiplied by a delta function which is

assumed to be centred at a in the asymptotic region where we know the asymptotic behaviour of the wavefunction. By the same token, equation (13) also can be rewritten in terms of the S matrix as

$$\langle\psi|\overleftarrow{L}|\psi\rangle = \langle I - O\mathbf{S}|\overleftarrow{L}|\psi\rangle = \langle I|\overleftarrow{L}|\psi\rangle = \langle I|\overleftarrow{L}|I\rangle - \langle I|\overleftarrow{L}|O\rangle\mathbf{S}. \tag{16}$$

On the other hand, using the ψ from equation (15) for the ket $|\psi\rangle$ of the third term in equation (16), we obtain

$$\langle\psi|\overleftarrow{L}|\psi\rangle = \langle I|\overleftarrow{L}(H+L-E)^{-1}L|I\rangle. \tag{17}$$

By combining equations (16) and (17), we finally obtain the expression for the S matrix as

$$\mathbf{S} = \frac{1}{\langle O|L|I\rangle}\{\langle I|L|I\rangle - \langle I|\overleftarrow{L}(H+L-E)^{-1}L|I\rangle\}. \tag{18}$$

Note again that $L = L(ik) = (1/2m)\,\delta(r-a)((\mathrm{d}/\mathrm{d}r) - ik)$ is used in equation (18).

This expression of equation (18) is of the form given by Manolopoulos *et al.* [17], obtained by converting the $\mathbf{Y}$ of equation (11) to the S matrix using the Wronskian relations. Also it is of the same form as classical Kapur–Peierls theory in which a homogeneous boundary condition basis set referenced to the scattering energy is used; in that case L can be omitted since the matrix elements of L are identically zero [12, 18]. However, equation (18) is a generalization of the above two earlier methods since any appropriate basis set $\{\phi_i; \phi_i(a) \neq 0$ for at least one $i\}$, including the ones used in the above two prior methods, can be used.

Equation (18) was derived directly through the use of the properties of the Bloch operator. It can be used with an energy independent inhomogeneous basis set, thus avoiding the recalculation of the basis set quantities at every energy as well as avoiding the 'slow convergence' problem caused by using a homogeneous basis set. It also automatically avoids the 'Kohn anomaly'.

The use of a few energy independent boundary functions referenced to several energies in the energy range of concern combined with energy independent truncated interior functions may be a viable alternative to the approach of Manolopoulos *et al.* [19]. They use one energy dependent real boundary function with a truncated set of interior functions (more precisely, $\mathscr{L}^2$ functions composed of contracted one-dimensional discrete eigenfunctions for each degree of freedom). This approach may be subject to spurious singularities caused by basis set linear dependence, and in addition a small number of the matrix elements have to be recalculated at each energy.

McCurdy *et al.* [7] also used several complex energy-independent boundary functions (corresponding to our ϕ_0) and analytical continuation in the infinite range case of equation (8) to reduce re-computation of interals for different energies.

4. Variational derivations

Thus far we have derived the general range expressions of S, K, and T matrices and the finite range expressions of Y, R, and S (in the context of R matrix theory) matrices, in terms of the Hamiltonian, the Bloch operator, and the proper wavefunction boundary conditions. They were derived with the method of moments which is non-variational.

However, specializing the general range expressions to the infinite range versions, we can still recover the conventional expressions which are variationally stable [6, 9,

17]. This indicates that the general range expressions of S, K, and T matrices derived above should be able to be derived variationally. This will be done in this section after some remarks regarding the variational derivations of the finite range Y, R, and S matrices in the context of R matrix theory.

4.1. *R matrix theory*

The finite range expressions for the Y, R, and S matrices can be derived using appropriate variation functionals. The variation functional for the Y matrix was given by Manolopoulos and Wyatt using their (0, 1) boundary condition basis set in [10]:

$$\frac{\mathbf{Y}}{2m} = \langle u_0|H+L-E|u_0\rangle + \langle u_0|H+L-E|\chi\rangle + \langle \chi|H+L-E|u_0\rangle + \langle \chi|H+L-E|\chi\rangle,$$

where the χ, a trial function, is expanded using the 'interior' basis $\{u_{i\neq 0}\}$, and $L = L(0)$.

The variation functional for the R matrix was given implicitly by Lane and Robson [20] as

$$\mathbf{F} \equiv \langle \psi|H+L-E|\psi\rangle - 2\langle \psi|L|\psi_{\text{exact}}\rangle,$$

where ψ_{exact} denotes the unknown exact wavefunction; but its presence will be cancelled out in the final expression. When ψ is the exact solution $-\mathbf{F}$ reduces to $\langle \psi_{\text{exact}}|L|\psi_{\text{exact}}\rangle$ or equivalently $1/2m\{\psi'_{\text{exact}}(a) - b\psi_{\text{exact}}(a)\}^2\mathbf{R}$. Lane and Robson pointed out that in the case of linear variation the final result is subject to error in the trial wavefunction in the first order. While this is true if the error is evaluated against the unknown exact value, the final expression obtained by the trial function is still stationary in the finite function space of the basis, and this is probably the best one can obtain with a stationary principle.

We do not present the details for these variational derivations since the Y matrix derivation was provided previously [10] and the R matrix derivation could be performed easily with a slight modification to the earlier derivation of [20] for the finite range S matrix calculations (i.e., changing the outgoing scattering boundary conditions to undefined ones, and in the last step cancelling the unknown exact values will give the variationally stable expression for the R matrix which is identical to equation (14)).

4.2. *S matrix*

Now we present the variational derivation of the general range S matrix expression. Conventionally, the Kohn variation functional for the S matrix, considering an infinite range, is presented as [1]

$$\mathbf{S} = \mathbf{S}_0 + i\langle \psi|H-E|\psi\rangle, \tag{19}$$

where ψ is assumed to be expanded as

$$\psi = I + \chi = I - O\mathbf{S}_0 + \sum_{i\neq 0} c_i\phi_i,$$

and thus $\mathbf{S}_0$ is the trial value of the S matrix. The stationary value is obtained by determining the ψ which extremizes the variation functional of equation (19); then the value $\mathbf{S}$ will be the variationally stable S matrix. However, this form of functional requires the outgoing function O as one of the basis functions, which we prefer to avoid, at least formally, in the general-range version.

An equivalent variation functional can be defined that is similar to the one used by Takatsuka and McKoy for the K matrix [21]. It is given by

$$\mathbf{F} \equiv -i\mathbf{S} = \langle I|H-E|I\rangle + 2\langle\chi|H-E|I\rangle + \langle\chi|H+L-E|\chi\rangle, \tag{20}$$

where we used

$$L\chi = L(ik)\chi = L(ik)(-O\mathbf{S}) = 0,$$

because $\chi \to -O\mathbf{S}$ asymptotically. Note that this differs from the usual functional only in the third term where the Bloch operator L is introduced. This L enforces the correct asymptotic boundary conditions when O is not included in the basis set, which is permitted for a finite range calculation.

The stationary property of equation (20) in the variation of the trial function ψ (or equivalently χ) in the vicinity of the exact solution ψ is verified easily as

$$\begin{aligned}\delta\mathbf{F} &= 2\langle\delta\chi|H-E|I\rangle + \langle\delta\chi|H+L-E|\chi\rangle + \langle\chi|H+L-E|\delta\chi\rangle \\ &= 2\langle\delta\chi|H-E|I+\chi\rangle = 0, \text{ to the first order in } \delta\chi,\end{aligned}$$

where we used the symmetry of the matrix representation of $H+L-E$. The extremization of the functional with respect to χ gives the trial function χ formally as

$$\frac{\partial\mathbf{F}}{\partial\chi} = 2(H-E)|I\rangle + \langle\chi|(H+L-E) + (H+L-E)|\chi\rangle = 0,$$

or

$$\chi = -(H+L-E)^{-1}(H-E)I,$$

where we used again the symmetry of the matrix representation of $H+L-E$. Substituting χ back to the original variation functional of equation (20) gives

$$-i\mathbf{S} = \langle I|H-E|I\rangle - \langle I|(\overleftarrow{H}-E)(H+L-E)^{-1}(H-E)|I\rangle,$$

which is the variationally stable expression for the S matrix and is *identical* to equation (8) derived non-variationally using the method of moments.

Note also that only L multiplied by unity guarantees the stationary property of the functional through the symmetry of the matrix representation of $H+L-E$. In the derivations using the method of moments, L may be multiplied by any constant. This indicates that in the application of the method of moments the best (i.e., stationary) results may be obtained with L alone as presented in section 3.

4.3. *K and T matrices*

Similar arguments can be made for variation functionals for K and T matrices modified with the proper Bloch operators leading to variationally stable expressions for K and T matrices. These lead to results identical to equations (9) and (10), respectively, which were derived non-variationally.

5. Novel variational derivations

Realizing the equivalence of the above two approaches (the method of moments and the variational derivation), we may conjecture that it could be possible to construct other variation functionals which are connected more directly to the method of moments than are the conventional functionals. Indeed, we can suggest a novel variation functional for each of the general range S, K, and T matrices and

finite range Y, R matrices. It is linear in the trial function rather than bilinear as in the conventional functionals, which has the readily visible direct relation with the method of moments. Below we detail the novel variational derivations.

5.1. *S, K, and T matrices*

For the S matrix, the linear variation functional may be given by ($L = L(ik)$)

$$\mathbf{F} \equiv -i\mathbf{S} = \langle I|H-E|I\rangle + \langle \bar{\chi}|H-E|I\rangle + \langle \chi|H-E|I\rangle + \langle \bar{\chi}|H+L-E|\chi\rangle, \quad (21)$$

where χ and $\bar{\chi}$ are the trial functions defined *independent* of each other. Note that the only change we made to the conventional functional (equation (20)) is partitioning of the trial functions into two formally independent functions. The stationary character of the functional of equation (21) in the variation of χ or $\bar{\chi}$ in the vicinity of the exact solution can be checked as

$$\begin{aligned}\delta(\mathbf{F})_{\chi} &= \langle \delta\chi|H-E|I\rangle + \langle \bar{\chi}|H+L-E|\delta\chi\rangle \\ &= \langle \delta\chi|H-E|I+\bar{\chi}\rangle = 0 \text{ to the first order in } \delta\chi,\end{aligned} \quad (22)$$

or

$$\begin{aligned}\delta(\mathbf{F})_{\bar{\chi}} &= \langle \delta\bar{\chi}|H-E|I\rangle + \langle \delta\bar{\chi}|H+L-E|\chi\rangle \\ &= \langle \delta\bar{\chi}|H-E|I+\chi\rangle = 0 \text{ to the first order in } \delta\bar{\chi},\end{aligned} \quad (23)$$

where we used the fact that

$$\langle \bar{\chi}|H+L-E|\delta\chi\rangle = \langle \delta\chi|H+L-E|\bar{\chi}\rangle,$$
$$L\bar{\chi} = 0, \quad L\chi = 0,$$

and the subscripts χ and $\bar{\chi}$ of the variation functional denote that the variation is done in that function while the other function is fixed. The trial functions which extremize the functional are given by, formally,

$$\frac{\partial \mathbf{F}}{\partial \chi} = (H-E)|I\rangle + \langle \bar{\chi}|(H+L-E) = 0,$$

$$\frac{\partial \mathbf{F}}{\partial \bar{\chi}} = (H-E)|I\rangle + (H+L-E)|\chi\rangle = 0,$$

or

$$\bar{\chi} = -(H+L-E)^{-1}(H-E)I, \quad (24)$$
$$\chi = -(H+L-E)^{-1}(H-E)I, \quad (25)$$

where we used the fact that

$$\langle \bar{\chi}|H+L-E|\phi_i\rangle = \langle \phi_i|H+L-E|\bar{\chi}\rangle \text{ for any } \phi_i.$$

Note that these extremization procedures to determine χ or $\bar{\chi}$ are identical to those of the method of moments (equations (4) and (5)).

Note also that, for example, the last two terms in equation (21) are cancelled exactly if the trial function $\bar{\chi}$ as determined by equation (24) is used as

$$\begin{aligned}&\langle \chi|H-E|I\rangle + \langle \bar{\chi}|H+L-E|\chi\rangle \\ &\quad = \langle \chi|H-E|I\rangle - \langle I|(\overleftarrow{H}-E)(H+L-E)^{-1}(H+L-E)|\chi\rangle \\ &\quad = \langle \chi|H-E|I\rangle - \langle I|\overleftarrow{H}-E|\chi\rangle = 0 \text{ identically},\end{aligned}$$

where we note that the operators $H+L-E$ and $(H+L-E)^{-1}$ are represented in the

same basis sets and symmetric. Then the back-substitution of the trial functions into equation (21) gives the variationally stable expression for the S matrix as

$$\begin{aligned} -i\mathbf{S} &= \langle I+\bar{\chi}|H-E|I\rangle \\ &= \langle I|H-E|I\rangle - \langle I|(\overleftarrow{H}-E)(H+L-E)^{-1}(H-E)|I\rangle, \end{aligned} \tag{26}$$

which is also identical to the final step in the application of the method of moments for the S matrix (equation (8)).

Similar modification to the conventional variation functional resulting in a form which is linear in the trial function can be used also to demonstrate the equivalence between the variational derivation and the method of moments for the K and T matrices.

5.2. *R matrix theory*

For the finite range matrices, the corresponding linear variation functional may be given by

$$\mathbf{Y} = \langle u_0|H+L-E|u_0\rangle + \langle u_0|H+L-E|\chi\rangle + \langle\bar{\chi}|H+L-E|u_0\rangle + \langle\bar{\chi}|H+L-E|\chi\rangle, \tag{27}$$

where $L = L(0)$ for the Y matrix and

$$-\langle\psi_{\text{exact}}|L|\psi_{\text{exact}}\rangle = \langle\psi|H+L-E|\bar{\psi}\rangle - \langle\psi|L|\psi_{\text{exact}}\rangle - \langle\bar{\psi}|L|\psi_{\text{exact}}\rangle \tag{28}$$

for the R matrix. In equations (27) and (28), χ, $\bar{\chi}$, ψ and $\bar{\psi}$ are, of course, the formally independent trial functions. Similar manipulations of equations (27) and (28) as for equation (21) show the direct one-to-one correspondence to the procedure of the method of moments in deriving the expressions for the Y, R (including the finite range S) matrices.

6. Conclusion

We had two aims in this paper: (1) to demonstrate that a wide variety of Kohn variational methods can be generalized by the appropriate use of the various Bloch operators $L(b)$ (i.e., with an appropriate argument for the 'b'), and (2) to show that variationally stable results can be derived using the method of moments, maintaining the symmetry of the expressions wherever possible (since this is also required by physical reasons such as the conservation of the probability or microscopic reversibility).

In the case of the S, K, and T matrices, which conventionally use infinite ranges for matrix element evaluations, the expressions are generalized to include the finite range case while still preserving the variationally stable character and possibly involving only one energy dependent function per channel in contrast to the two functions for the infinite range calculations. We pointed out that the K matrix can be calculated without encountering any 'spurious singularities' in these finite range calculations.

For the Y and R (including the finite range S) matrices which are inherently defined for a finite range, inhomogeneous basis sets can be used by virtue of the Bloch operator. This results in rapid convergence, in contrast to the conventional homogeneous basis set approach, which shows notoriously slow convergence without a suitable correction such as that of Buttle [22].

The actual derivations were accomplished first through the applications of the method of moments, which is much simpler to use than the conventional variational principles involving bilinear functionals. The variationally stable characters of these

general range expressions were subsequently confirmed by re-derivations using the proper variation functionals modified with the Bloch operator. The direct one to one correspondence between the method of moments and the variational principle was demonstrated through the introduction of a novel variation functional which is linear in the trial functions.

Finally, we note one disadvantage of the above approach for particular types of problem. For multi-arrangement reactive scattering, there is a subtle disadvantage when the Bloch operator is used in the expressions. The natural coordinate systems are often the Jacobi coordinate systems referenced to each arrangement channel, and the Bloch operator contains the projection operators composed of the internal states expressed in these different Jacobi coordinates. This necessitates the use of basis sets composed of functions defined in each set of Jacobi coordinates for accurate calculations [17, 19]. In these cases, exchange-type overlap integrals (i.e., between the functions defined in two different coordinates) have to be evaluated, which requires demanding computation. In addition, some redundancy of the basis functions is common, especially for the interaction region. Although no such disadvantages arise for single arrangement problems, further methodological developments are needed if we are to utilize the Bloch operator efficiently in applications to general molecular reactive scattering problems.

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