# A NEW VARIATIONAL EXPRESSION FOR THE SCATTERING MATRIX

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*Dedicated to Dr R. Zahradník on the occasion of his 60th birthday.*

The **S**-matrix version of the Kohn variational method is used to obtain a new, more concise expression for the scattering matrix, one that has both esthetic and practical advantages over earlier ones that have been used.

*I wish to take the opportunity to extend my best wishes to Dr Rudolf Zahradník. It has been both a personal and a scientific pleasure to have had the privilege of knowing him over the last ten years.*

It has recently been realized[1] that the Kohn-variational approximation[2,3] to quantum mechanical scattering does not give equivalent results when it is applied to the **K**-matrix (i.e., real, standing wave boundary conditions) or to the **S**-matrix (i.e., complex, incoming/outgoing wave boundary conditions). Furthermore, the **S**-matrix version of the Kohn method is free of the "Kohn-anomalies"[3] that have plagued the commonly used **K**-matrix version and made it unsatisfactory for general use. The **S**-matrix version, on the other hand, has been seen to be well-behaved and efficient.[1,4] It is particularly useful for quantum scattering calculations of chemical reactions,[4] because the non-local (i.e., exchange) character[5-7] of reactive scattering negates the use of standard propagation methods[8,9] for solving the coupled-channel scattering equations. The important practical feature of the **S**-matrix version of the Kohn method is that it requires calculation of matrix elements only of the Hamiltonian operator itself, and not those involving a Green's function for a reference problem.

In this paper I explore further the formal structure of the **S**-matrix version of the Kohn method and cast it in an even more useful form for practical scattering calculations.

## *Equivalence of Variational Green's Function and S-matrix Kohn*

It is first useful to demonstrate explicitly that the variational approximation for the Green's function[10,11], $G^{(+)}(E) \equiv (E + i\varepsilon - \mathbf{H})^{-1}$, that was used before,[1] is indeed

equivalent to the **S**-matrix version of the Kohn variational method.[2,3] The specific equations below will all refer to the simple case of *s*-wave potential scattering, but they are readily generalizable to the interesting case of inelastic and reactive scattering (as in Ref. 1).

The expression obtained by Miller and Jansen op de Haar[1] for the **S**-matrix is

$$\mathbf{S} = e^{2i\eta} - (8\pi i/\hbar)\,[\langle\chi|V_1|\,\chi\rangle - \\ - \sum_{l,l'=1}^{N} \langle\chi|V_1|\,u_l\rangle\,(\langle u_l|\mathbf{H} - E|\,u_{l'}\rangle)^{-1}\,\langle u_{l'}|V_1|\,\chi\rangle]\,, \tag{1}$$

where $\chi$ is the scattering wave function for the reference potential $V_0$, with asymptotic form

$$\chi(r) \sim e^{i\eta} \sin(kr + \eta)/v^{1/2}\,, \tag{2}$$

$v = \hbar k/(2\pi m)$, and $\eta$ is the phase shift for $V_0$; $V_1$ is the residual potential (i.e., $V \equiv V_0 + V_1$ is the total potential). The basis functions $\{u_l\}$ for $l = 2, \ldots, N$ are a real, square-integral set, while $u_1(r)$ is the special basis function which describes the outgoing wave boundary conditions inherent in $G^{(+)}(E)$ (see Ref. 1); $u_1(r)$ is regular at $r = 0$ and must have the asymptotic form

$$u_1(r) \sim e^{ikr}/v^{1/2} \tag{3}$$

and is usually chosen in the form

$$u_1(r) = e^{ikr} f(r)/v^{1/2}\,, \tag{4}$$

where $f(r)$ is a cut-off function to make $u_1(r)$ vanish at $r = 0$ (e.g., $f(r) = (1 - e^{-\alpha r})$). Also, all matrix elements in Eq. (*1*) and throughout the paper are without complex conjugation of the "bra" wavefunction; thus the matrix $\langle u_l|\mathbf{H} - E|\,u_{l'}\rangle$ is a complex symmetric matrix. The notation $(\langle u_l|\,|u_{l'}\rangle)^{-1}$ in Eq. (*1*) is short-hand for the $(l, l')$ element of the matrix whose inverse is $\langle u_l|\,|u_{l'}\rangle$.

For present purposes it is useful to note that Eq. (*1*) can also be expressed equivalently as

$$\mathbf{S} = e^{2i\eta} - (8\pi i/\hbar)\,\mathrm{ext}\,\{\langle\chi|V_1|\,\chi\rangle + 2\sum_{l=1}^{N} c_l\langle u_l|V_1|\,\chi\rangle + \\ + \sum_{l,l'=1}^{N} c_l c_{l'}\langle u_l|\mathbf{H} - E|u_{l'}\rangle\}\,, \tag{5}$$

where ext { } means the *extremum* with respect to varying the coefficients $\{c_l\}$. It is a trivial matter to show this equivalence: the equations

$$\frac{\partial}{\partial c_l}\{\ \} = 0 \tag{6}$$

lead to linear equations for the coefficients which, when solved for and substituted into Eq. (5), lead to Eq. (1). It is also useful to note that Eq. (5) corresponds to the following scattering wavefunction,

$$\psi(r) = \chi(r) + \sum_{l=1}^{N} c_l u_l(r)\,. \tag{7}$$

Eqs (5)–(7) are now compared to the **S**-matrix version of the Kohn variational principle,[1,2] which gives the **S**-matrix as

$$\boldsymbol{S} = \text{ext}\,\{e^{2i\eta} + 2ic_1 - (8\pi i/\hbar)\langle\psi|\mathbf{H} - E|\,\psi\rangle\}\,, \tag{8}$$

where the trial wavefunction is given by Eq. (7), and ext { } again means extremum with respect to the coefficients $\{c_l\}$. (The terms $e^{2i\eta} + 2ic_1$ in Eq. (8) constitute the "trial **S**-matrix" in the language of the Kohn method;[2] i.e., the asymptotic form of the trial function of Eq. (7) is

$$\begin{aligned}\psi(r) &\sim [e^{i\eta}\sin(kr + \eta) + c_1\, e^{ikr}]/v^{1/2} \sim \\ &\sim [-e^{-ikr} + e^{ikr}(e^{2i\eta} + 2ic_1)]\,(2iv^{1/2})^{-1}\end{aligned} \tag{9}$$

which identifies $(e^{2i\eta} + 2ic_1)$ as the trial **S**-matrix.) Substituting Eq. (7) into (8) gives the explicit form

$$\begin{aligned}\boldsymbol{S} = e^{2i\eta} - (8\pi i/\hbar)\,\text{ext}\,\{&-\hbar c_1/(4\pi) + \langle\chi|\mathbf{H} - E|\,\chi\rangle + \\ &+ \sum_{l,l'=1}^{N} c_l c_{l'}\langle u_l|\mathbf{H} - E|\,u_{l'}\rangle + 2\sum_{l=2}^{N} c_l\langle u_l|\mathbf{H} - E|\,\chi\rangle + \\ &+ c_1(\langle\chi|\mathbf{H} - E|\,u_1\rangle + \langle u_1|\mathbf{H} - E|\,\chi\rangle)\}\,,\end{aligned} \tag{10}$$

where the fact has been used that

$$\langle u_l|\mathbf{H} - E|\,\chi\rangle = \langle\chi|\mathbf{H} - E|\,u_l\rangle \tag{11}$$

for $l \geqq 2$; this is true because $u_l(r) \to 0$ as $r \to \infty$ for $l \geqq 2$. Eq. (11) is not true for $l = 1$, however, because $u_1(r)$ does not vanish at $r \to \infty$. Integration by parts, in fact, gives the result

$$\langle\chi|\mathbf{H} - E|\,u_1\rangle = \langle u_1|\mathbf{H} - E|\,\chi\rangle - (\hbar^2/8\pi^2\mu)\,(\chi u_1' - \chi' u_1\rangle|_0^\infty$$

and with $\chi(r)$ and $u_1(r)$ as given above, this is

$$\langle\chi|\mathbf{H} - E|u_1\rangle = \langle u_1|\mathbf{H} - E|\chi\rangle + \hbar/(4\pi) . \tag{12}$$

Using Eq. (2), and also the fact that

$$(\mathbf{H} - E)|\chi\rangle = V_1|\chi\rangle , \tag{13}$$

Eq. (10) becomes identical to Eq. (5) (which is equivalent to Eq. (1)), which was the goal of this Section, i.e., to show that the **S**-matrix version of the Kohn variational method, Eqs (7) and (8), is equivalent to Eq. (1), the result obtained before[1] from the variational approximation to the Green's function. Note that it is the surface term in Eq. (12) that cancels the "extra term", $-\hbar c_1/(4\pi)$, in Eq. (10).

*A New Expression for the* **S***-matrix*

Having established the equivalence of the **S**-matrix version of the Kohn method to the variational approximation to $G^{(+)}$, I now use the Kohn method to obtain a new expression for the **S**-matrix. The motivation is to obtain a more symmetrical form for the **S**-matrix, and also a more computationally useful expression.

The new result is obtained by using a trial function $\psi$ and that treats incoming and outgoing waves on an equal footing, namely

$$\psi(r) = -u_0(r) + \sum_{l=1}^{N} c_l u_l(r) , \tag{14}$$

where $u_1(r)$ is as before, Eq. (4), and $u_0(r)$ is a corresponding cut-off incoming wave,

$$u_0(r) = \mathrm{e}^{-\mathrm{i}kr} f(r)/v^{1/2} \tag{15a}$$

$$= u_1(r)^* . \tag{15b}$$

The functions $\{u_l(r)\}$, $l \geqq 2$, are, as before, short range, square-integrable functions that may be taken to be real. In terms of $\psi$ of Eq. (14) the Kohn expression for the **S**-matrix is

$$\mathbf{S} = \mathrm{ext}\,\{c_1 + (2\pi\mathrm{i}/\hbar)\langle\psi|\mathbf{H} - E|\psi\rangle\} , \tag{16}$$

where the constants appearing here are different from those of the previous section, e.g., Eq. (8), because the trial wavefunction of Eq. (14) is normalized differently.

Apart from the symmetry between terms $\mathrm{e}^{+\mathrm{i}kr}$ and $\mathrm{e}^{-\mathrm{i}kr}$ in the trial wavefunction of Eq. (14), it also has the advantage that one need not calculate the distorted wave-

function $\chi$ for some reference potential. The main reason for using a distorted function before,[1,4] rather than a plane wave $\chi(r) \to \sin(kr)/v^{1/2}$, is so that the classically forbidden region of a repulsive potential need not be spanned by the real basis functions $\{u_l(r)\}$, $l \geqq 2$. (If one used $\psi(r)$ of Eq. (7) with $\chi(r)$ a plane wave, then the real basis $\{u_l\}$, $l \geqq 2$, would have to span the classically forbidden region in order to cancel the plane wave in this region, because the true wavefunction $\psi$ is zero there.) Other than this, there is little reason to use a distorted wave $\chi$. For the present trial wavefunction, Eq. (14), there is no need for the real basis to span the classically forbidden repulsive core, because $u_0$ and $u_1$ vanish there by virtue of the cut-off function $f(r)$.

Returning to Eqs (14)–(16), substitution of Eq. (14) into Eq. (16) gives

$$\begin{aligned} \mathbf{S} = (2\pi\mathrm{i}/\hbar)\,\mathrm{ext}\,\{ & -\mathrm{i}\hbar c_1/(2\pi) + \langle u_0|\mathbf{H} - E|\,u_0\rangle + \\ & + \sum_{l,l'=1}^{N} c_l c_{l'} \langle u_l|\mathbf{H} - E|\,u_{l'}\rangle + 2\sum_{l=2}^{N} c_l \langle u_l|\mathbf{H} - E|\,u_0\rangle + \\ & + c_1(\langle u_1|\mathbf{H} - E|\,u_0\rangle + \langle u_0|\mathbf{H} - E|\,u_1\rangle)\}\,, \end{aligned} \tag{17}$$

where the fact has been used that

$$\langle u_0|\mathbf{H} - E|\,u_l\rangle = \langle u_l|\mathbf{H} - E|\,u_0\rangle \tag{18}$$

for $l \geqq 2$. For $l = 1$, though, integration by parts gives

$$\langle u_0|\mathbf{H} - E|\,u_1\rangle = \langle u_1|\mathbf{H} - E|\,u_0\rangle - \mathrm{i}\hbar/(2\pi) \tag{19}$$

so that Eq. (17) becomes

$$\begin{aligned} \mathbf{S} = (2\pi\mathrm{i}/\hbar)\,\mathrm{ext}\,\{ & \langle u_0|\mathbf{H} - E|\,u_0\rangle + 2\sum_{l=1}^{N} c_l \langle u_l|\mathbf{H} - E|\,u_0\rangle + \\ & + \sum_{l,l'=1}^{N} c_l c_{l'} \langle u_l|\mathbf{H} - E|\,u_{l'}\rangle\}\,. \end{aligned} \tag{20}$$

Varying the coefficients $\{c_l\}$, $l = 1, \ldots, N$, to extremize Eq. (20) leads to the usual linear equations which, when solved and put back into Eq. (20), gives the following variational result for the $\mathbf{S}$-matrix,

$$\mathbf{S} = (2\pi\mathrm{i}/\hbar)\,(\mathbf{M}_{0,0} - \underline{\mathbf{M}}_0^{\mathrm{T}} \cdot \underline{\underline{\mathbf{M}}}^{-1} \cdot \underline{\mathbf{M}}_0)\,, \tag{21}$$

where

$$\mathbf{M}_{0,0} = \langle u_0|\mathbf{H} - E|\,u_0\rangle$$

$$(\underline{\mathbf{M}}_0)_l = \langle u_l|\mathbf{H} - E|\,u_0\rangle$$

$$(\underline{\underline{M}})_{l,l'} = \langle u_l | \mathbf{H} - E | u_{l'} \rangle \,.$$

The final result is obtained by noting that Eq. (*21*) is an example of the matrix partitioning identity; if a matrix $\underline{\underline{M}}$ is partitioned into $P$ and $Q$ blocks, then this identity is

$$(\boldsymbol{M}^{-1})_{P,P} = [\boldsymbol{M}_{P,P} - \boldsymbol{M}_{P,Q}(\boldsymbol{M}_{QQ})^{-1}\, \boldsymbol{M}_{Q,P}]^{-1} \,. \tag{22}$$

Identifying $P$ with the one dimensional block $l = 0$, and $Q$ with the block $l = 1, \ldots, N$, Eq. (*22*) shows that Eq. (*21*) can also be written as

$$\boldsymbol{S} = (2\pi \mathrm{i}/\boldsymbol{h})\, [(\underline{\underline{\boldsymbol{M}}}^{-1})_{0,0}]^{-1} \,, \tag{23}$$

where here $\underline{\underline{\boldsymbol{M}}}$ is the $(N + 1)$ dimensional matrix.

$$\boldsymbol{M}_{l,l'} = \langle u_l | \mathbf{H} - E | u_{l'} \rangle \tag{24a}$$

$l, l' = 0, \ldots, N$, with the exception that

$$\boldsymbol{M}_{0,1} \equiv \boldsymbol{M}_{1,0} = \langle u_1 | \mathbf{H} - E | u_0 \rangle \,. \tag{24b}$$

Eqs (*23*) and (*24*) are the new, extremely concise expression for the $\boldsymbol{S}$-matrix. It involves only matrix elements of $(\mathbf{H} - E)$ in the $\{u_l\}$, $l = 0, \ldots, N$ basis. There is no zeroth order $\boldsymbol{S}$-matrix, as in Eq. (*1*), that refers to a reference problem, just as there is no distorted wavefunction for a reference.

Though Eq. (*23*) is the most compact expression for the $\boldsymbol{S}$-matrix, in practice it is probably best to separate the complex part of the matrix $\underline{\underline{\boldsymbol{M}}}$ from the real part. To invert $\underline{\underline{\boldsymbol{M}}}$ as needed in Eq. (*23*) one can thus partition $\underline{\underline{\boldsymbol{M}}}$ via Eq. (*22*) but where $P$ is $l = 0, 1$ and $Q$ is $l = 2, \ldots, N$. This gives

$$\boldsymbol{S} = (2\pi \mathrm{i}/\boldsymbol{h})\, (\boldsymbol{N}_{0,0} - \boldsymbol{N}_{1,0}^2/\boldsymbol{N}_{1,1}) \,, \tag{25}$$

where

$$\boldsymbol{N}_{l,l'} = \boldsymbol{M}_{l,l'} - \underline{\boldsymbol{M}}_l^{\mathrm{T}} \cdot \underline{\underline{\boldsymbol{M}}}^{-1} \cdot \boldsymbol{M}_{l'} \tag{26}$$

for $l, l' = 0, 1$, and where in Eq. (*26*) $\underline{\boldsymbol{M}}_0$ and $\underline{\boldsymbol{M}}_1$ are $(N - 1)$ dimensional vectors and $\underline{\underline{\boldsymbol{M}}}$ an $(N - 1)$ dimensional (real-valued) matrix

$$(\underline{\boldsymbol{M}}_0)_l = \langle u_l | \mathbf{H} - E | u_0 \rangle \tag{27a}$$

$$(\underline{\boldsymbol{M}}_1)_l = \langle u_l | \mathbf{H} - E | u_1 \rangle \tag{27b}$$

$$(\underline{\underline{\boldsymbol{M}}})_{l,l'} = \langle u_l | \mathbf{H} - E | u_{l'} \rangle \tag{27c}$$

$l, l' = 2, \ldots, N$. One also notes the simplifying facts that

$$\underline{\boldsymbol{M}}_1 = \underline{\boldsymbol{M}}_0^* \tag{28a}$$

$$\boldsymbol{M}_{1,1} = \boldsymbol{M}_{0,0}^* \tag{28b}$$

$$\mathrm{Im}\, \boldsymbol{M}_{1,0} = \boldsymbol{h}/(4\pi) . \tag{28c}$$

*Concluding Remarks*

Eqs (*23*) and (*24*) – or their partitioned form, Eqs (*25*)–(*27*) – provides an extremely straight-forward computational procedure, and it is expected to be at least as efficient as the earlier calculations[1,4] based on (the multichannel version of) Eq. (*1*).

In concluding it may be noted that distorted wave-like information can be included in these equations through the functions $u_0$ and $u_1 = u_0^*$. Thus it is required only that these functions be regular (i.e., vanish) at $r = 0$, and have the asymptotic form

$$\left.\begin{matrix} u_0(r) \\ u_1(r) \end{matrix}\right\} \sim \mathrm{e}^{\mp \mathrm{i}kr}/v^{1/2} . \tag{29}$$

To include distorted wave-like in formation in the trial wavefunction one determines the (irregular) solutions for some reference potentive $V_0(r)$ that have the asymptotic forms in Eq. (*29*). For example, one begins at large $r$ with

$$u_0(r) = \mathrm{e}^{-\mathrm{i}kr}/v^{1/2} \tag{30}$$

and integrates the reference Schrödinger equation *inward*. If $\tilde{u}_0(r)$ is the function so obtained, then

$$u_0(r) = \tilde{u}_0(r) f(r) , \tag{31}$$

where $f(r)$ is a cut-off function; the function $u_1(r)$ is then

$$u_1(r) = u_0(r)^* . \tag{32}$$

It is also possible to employ this approach with a *multi-channel* reference.[12–14]

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