

## Volume-Bloch Operator Approach to Quantum Reactive Scattering on Non-orthogonal Scattering Coordinates<sup>†</sup>

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The most detailed observables in theoretical studies of chemical reactions are the quantum state-to-state reaction probabilities determined as the modulus squared of the scattering matrix (S matrix) elements. Quantum mechanical methodology for S matrix calculation is well developed, especially in the level of Born-Oppenheimer approximation used for separating the nuclear dynamics from electronic motions. One of such numerical methods adopts boundary value Bloch operator in setting up the basis set representation of Schrödinger equation for the nuclear dynamical solution in the continuum region of energy (scattering energy) such as in the log derivative Kohn variational principle (Y-KVP) method of Manolopoulos and Wyatt.<sup>1</sup> It has virtues of "totally energy-independent and real-valued basis functions/intermediate integrals" up to the point just before the final complex-valued S matrix evaluation. Since one must investigate the scattering solutions for many energies in the general practice of scattering problem, these properties substantially increase the computational efficiency than otherwise.

However, when applied for general reactive multi-arrangement scattering on non-orthogonal coordinate system (e.g., the well-known collinear H<sub>2</sub>+H reactive scattering), it turns out to be inevitable to adopt wasteful redundant basis sets, each of which suitable for entrance and exit channels (at least, in the primitive direct product basis set description), and the subsequent cumbersome exchange-type integrations between the functions defined on different coordinate systems are unavoidable (about half of the integrals are of this type for the above example).<sup>1,2</sup> Such formal inefficiency in the Y-KVP method can be avoided in the S-matrix version of Kohn variational principle (S-KVP) method by replacing the real-valued and energy-independent continuum-type basis functions with complex-valued and energy-dependent ones.<sup>3</sup> However, it accompanies adverse effects, i.e., making a small rectangular part of Hamiltonian matrix to be complex-valued and energy-dependent.

This work was motivated by noting that a delta function is included in the definition of conventional Bloch operator, consequently, it becomes a surface operator in multi-dimensional problem.<sup>2</sup> By changing the effective region of the

Bloch operator from surface to volume, we might hope to remove such unfavorable features of the Y-KVP method in a different way, and we intend to pursue this idea further. In the long run, no redundant basis sets are needed and all basis functions are real-valued and energy-independent, subsequently most of the intermediate integrals are real-valued and energy-independent except N<sub>open</sub> (the number of open channels) integrals which are complex-valued and energy-dependent in the present approach. All such features add up to suggest better performance over both of the Y-KVP and S-KVP methods, at least formally. Unfortunately, a small rectangular Bloch-operator-related matrix becomes complex-valued (though it can be evaluated from energy-independent intermediate integrals) just like in the S-KVP method. Perhaps, more importantly, it is a pity that this method is not benefited from the variational property, thus the calculated numerical S matrix is not guaranteed to be symmetric, unlike in the Y-KVP and S-KVP methods, as a result, it might be suffered from unstable features.

Now we detail the derivation of the present approach. Scattering wave function  $\psi$  is chosen to satisfy the usual S-matrix boundary condition in the asymptotic region as a linear combination of incoming (I) and outgoing (O) waves with S matrix as the expansion coefficient,

$$\psi \rightarrow I - OS. \quad (1)$$

For simplicity, we use one-dimensional s-wave scattering problem on the radial  $r$  coordinate, unless otherwise noted. The Schrödinger equation for  $\psi$  with the Hamiltonian operator  $\hat{H}$  and the scattering energy  $E$ , along with the boundary condition implied by Eq. (1) can be written as

$$[\hat{H} - E]|\psi\rangle = 0, \quad (2)$$

$$\delta(r-p)(\hat{D} - Y)|\psi - I\rangle = 0, \quad (3)$$

$$\hat{D} = \frac{\hbar^2}{2m} \frac{d}{dr}, \quad Y = \frac{\hbar^2}{2m} \frac{O'}{O},$$

where the unit-flux normalized incoming and outgoing waves are,

$$I = \sqrt{\frac{m}{\hbar k}} e^{-ikr} \text{ and } O = \sqrt{\frac{m}{\hbar k}} e^{ikr},$$

and the  $m$ ,  $k$ , and  $Y$  are the particle reduced mass, wave-number, and a quantity proportional to the log derivative of

<sup>†</sup>This paper is dedicated to Professor Kook Joe Shin on the occasion of his honourable retirement

outgoing wave  $O$ , respectively. Also, the point  $p$  is located in the asymptotic region. The operator including the delta function in Eq. (3) can be considered as “surface-Bloch operator” in our present point of view.

The linear expansion of  $\psi$  by real-valued and energy-independent  $L^2$  (square integrable) basis functions  $u_i$ 's is given by

$$\psi = \sum_{i=0}^{N_{\text{basis}}} C_i u_i. \quad (4)$$

The corresponding basis set is defined on a finite range  $[0, p]$  and composed of two subsets; one is termed “interior basis” and composed of  $N_{\text{basis}}$  basis functions which satisfy,  $u_{i \neq 0}(0)=0$ ,  $u_{i \neq 0}(p)=0$ , and the other includes the so called “boundary function” which satisfies,  $u_0(0)=0$ ,  $u_0(p)=1$ . We combine Eqs. (2), (3) and transform them into a linear system of equations by projecting them onto basis functions as follows using Galerkin's method,<sup>4</sup>

$$\langle u_i | \hat{H} - E | \psi \rangle + \langle u_i | \delta(r-p)(\hat{D}-Y) | \psi - I \rangle = 0,$$

which is equivalent to,

$$\langle u_0 | \hat{H} + \delta(r-p)(\hat{D}-Y) - E | \psi \rangle = \langle u_0 | \delta(r-p)(\hat{D}-Y) | I \rangle, \quad (5)$$

$$\langle u_i | \hat{H} - E | \psi \rangle = 0, \text{ for } i \neq 0. \quad (6)$$

The final solution of Eqs. (4)-(6) turns out to be identical to the one obtained by Y-KVP method which involves a Hamiltonian-related symmetric coefficient matrix for  $C_i$ 's and the solution is variationally stable.<sup>2</sup>

We modify the conventional Y-KVP method by replacing  $\delta(r-p)$  with  $\lim_{\alpha \rightarrow \infty} \alpha \tilde{g}(r-p)$  in Eq. (5) while keeping Eq. (6) intact. Then, Eq. (5) is transformed to

$$\langle u_0 | \tilde{g}(r-p)(\hat{D}-Y) | \psi \rangle = \langle u_0 | \tilde{g}(r-p)(\hat{D}-Y) | I \rangle.$$

Next, we replace  $u_0 \tilde{g}(r-p)$  with  $g(r-p)$  to obtain

$$\langle g(r-p) | (\hat{D}-Y) | \psi \rangle = \langle g(r-p) | (\hat{D}-Y) | I \rangle, \quad (7)$$

where  $g(r-p)(\hat{D}-Y)$  is termed “volume-Bloch operator” and introduced by us for the first time to our best knowledge. The  $g(r-p)$  is chosen as real-valued and a bell shape function centered at  $r=p$  in the asymptotic region to ensure the validity of Eq. (1) (or, equivalently, Eq. (3)) which effectively imposes the proper boundary condition on  $\psi$ . Also, the outer boundary of the basis function definition range should be properly extended to accommodate the effective region of the volume-Bloch operator, thus  $p$  in Eq. (7) is no longer equal to the outer boundary of Eq. (4) but located inside the range.

The Eqs. (4), (6), and (7) constitute a novel form of linear system of inhomogeneous equations for the expansion coefficients  $C_i$ 's which is our main results of the present approach. This system of equations can be cast into the matrix-vector form for the coefficients  $C_i$ 's, as follows,

$$MC = I, \quad (8)$$

where the elements of matrices are

$$M_{0i} = \langle g(r-p) | (\hat{D}-Y) | u_i \rangle, \quad M_{i \neq 0, j \neq 0} = \langle u_i | \hat{H} - E | u_j \rangle, \\ I_{00} = \langle g(r-p) | (\hat{D}-Y) | I \rangle.$$

To obtain a working equation to be used for the  $S$  matrix extraction, we operate the volume-Bloch operator with  $Y^*$  (instead of  $Y$ ) on the particular scattering wave function  $\psi$  satisfying Eq. (1) in the asymptotic region (around  $r=p$ ) as follows,

$$\begin{aligned} \langle g(r-p) | (\hat{D}-Y^*) | \psi \rangle &= -\langle g(r-p) | (\hat{D}-Y^*) | O \rangle S \\ &= -\langle g(r-p) | (\hat{D}-Y) | I \rangle^* S. \end{aligned} \quad (9)$$

The LHS of Eq. (9) is further simplified by expanding  $\psi$  according to Eq. (4), and noting that the basis functions are real-valued, we get

$$\sum_{i=0}^{N_{\text{basis}}} \langle g(r-p) | (\hat{D}-Y) | u_i \rangle^* C_i = -\langle g(r-p) | (\hat{D}-Y) | I \rangle^* S, \quad (10)$$

where we also note that the intermediate integrals used to set up Eq. (8) appear again, thus no additional integration is needed.

The  $S$  matrix is simply given by inverting Eq. (10) for  $S$ . In multi-dimensional problem,  $u_0$  basis function should be augmented to accommodate all the open channels properly at the specific scattering energy, and is given by

$$S = -(I_{00}^*)^{-1} M_{01}^* M^{-1} I, \quad (11)$$

where  $I_{00}$  and  $M_{01}$  are square and rectangular part of  $I$  and  $M$  matrices appeared in Eq. (8), respectively, corresponding to the rows of open channels only. The properties of the matrices  $I_{00}$ ,  $M_{01}$ ,  $M$ ,  $I$  are complex-, complex-, mostly real- and complex-valued, respectively. And, their sizes are,  $N_{\text{open}} \times N_{\text{open}}$ ,  $N_{\text{open}} \times (N_{\text{open}} + N_{\text{basis}})$ ,  $(N_{\text{open}} + N_{\text{basis}}) \times (N_{\text{open}} + N_{\text{basis}})$ ,  $(N_{\text{open}} + N_{\text{basis}}) \times N_{\text{open}}$ , respectively. Also, the intermediate integrals used for calculating these matrices are energy-dependent, -independent, -independent, and energy-dependent, respectively.

Note that the elements of  $I$  are zeroes except  $N_{\text{open}}$  elements (each corresponding to a specific boundary condition) located along the diagonal of a certain square portion of this matrix. By taking advantage of the sparsity of  $I$ , the matrix inversion in Eq. (11) can be done more efficiently using partitioned matrix inversion technique after partitioning  $M$  according to the basis function types (i.e., by noting whether the row/column indices of the submatrix correspond to interior or boundary functions).<sup>1,3</sup> Moreover, if the Hamiltonian matrix composing the submatrix  $M_{11}$  (corresponding to interior basis only), whose elements are real-valued and energy-independent, is diagonalized in advance, we could save substantial CPU times, especially for many-scattering-energy calculation because the matrix inversion process reduces to much simpler matrix multiplications involving eigen-solutions of the Hamiltonian matrix.

## Calculation Results

The present method as summarized in Eq. (11) is applied

to the reactive scattering model of collinear  $\text{H}_2+\text{H}$  reaction which is simple but not trivial. We use the familiar LSTH potential energy surface and mass-scaled Jacobi coordinates to represent the Hamiltonian operator.<sup>5</sup> This model has been examined previously by us and others (e.g., see references 6, 7).

The volume-Bloch operator and the boundary functions are defined on the coordinates corresponding to their proper arrangement channels which are mass-scaled Jacobi coordinates for entrance and exit channels. For the interior basis functions, we use two-dimensional primitive direct product of DVR<sup>7</sup> based on the 1-dimensional particle-in-a-box eigenfunctions defined on the normal coordinates of the transition state, one of whose axis bisects equally the entrance and exit channel directions. Before setting up Eq. (11), the above primitive basis sets are trimmed according to the criteria of nuclear configuration, channel-radius and potential-energy-cut.<sup>7</sup> As seen in Figure 1, the skew angles between two axes of scattering coordinates corresponding to arrangement channels are  $60^\circ$ , thus the entrance and exit channels are not orthogonal.

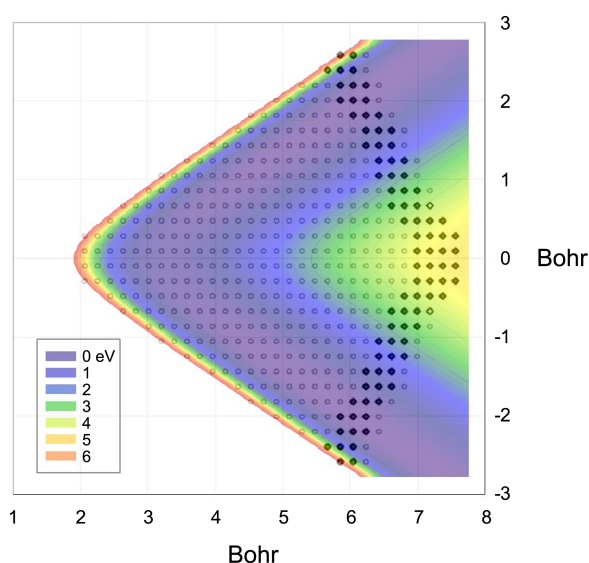
The inhomogeneity noted in Eq. (7) could be visible only when the incoming wave entrance channel asymptotic region coincides with the location of volume-Bloch operator, otherwise it vanishes, i.e., we have

$$\langle G_\alpha(R_\alpha, r_\alpha) | (\hat{D}_\alpha - Y_\alpha) | \psi_\gamma \rangle = \langle G_\alpha(R_\alpha, r_\alpha) | (\hat{D}_\alpha - Y_\alpha) | I_\gamma \rangle \delta_{\alpha\gamma}. \quad (12)$$

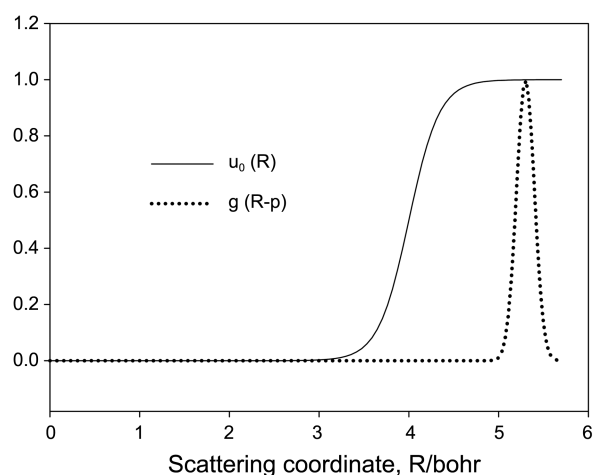
The asymptotic bell shape function  $G_\alpha(R_\alpha, r_\alpha)$  is a generalization of  $g(r-p)$  to the present two-dimensional case,

$$G_\alpha(R_\alpha, r_\alpha) = g_\alpha(R_\alpha - p_\alpha) \varphi_\alpha(r_\alpha), \quad (13)$$

where  $R_\alpha$ ,  $p_\alpha$  denote the scattering coordinate (one of the mass-scaled Jacobi coordinate describing scattering process) and the center of the volume-Bloch operator for  $\alpha$ -channel,



**Figure 1.** Schematic representation of contours of LSTH potential energy surface cut for collinear reaction, locations of DVR basis function centers denoted by open circles, and region of bell shape functions denoted by diamonds superimposed on the DVR basis centers for a typical calculation.

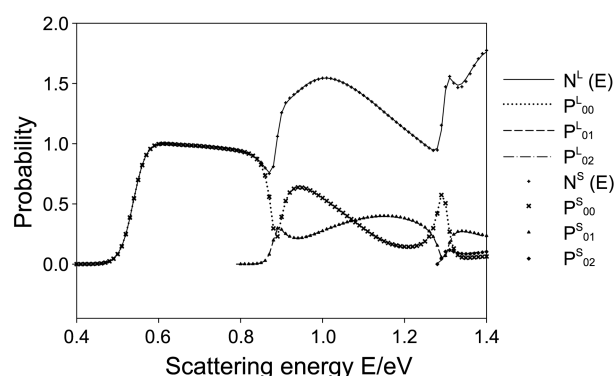


**Figure 2.** Boundary function  $u_0(R)$  and bell shape function  $g(R-p)$  for a typical calculation where the outer boundary set at 5.7 bohr.

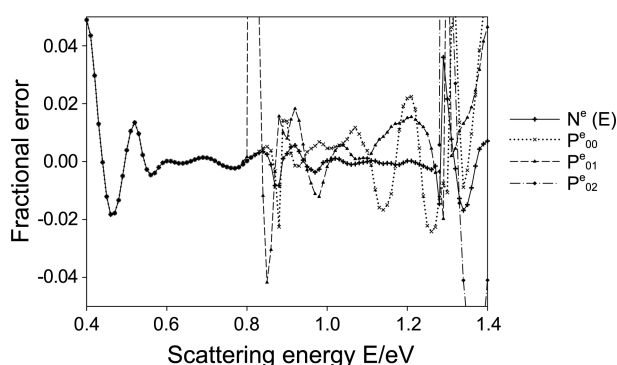
respectively. Also, the subscript  $\alpha$  may indicate a composite quantum number of both the arrangement channel and the isolated  $\text{H}_2$  molecular vibrational state  $\varphi_\alpha(r_\alpha)$  where appropriate.

Schematic representation of the collinear cross section of LSTH potential energy surface, and the locations of trimmed DVR basis function centers, and the region of bell shape function  $G_\alpha(R_\alpha, r_\alpha)$  are presented in Figure 1. The boundary function  $u_0(R)$  and bell shape function  $g(R-p)$  can be seen in Figure 2 for a typical calculation.

We show in Figure 3 the calculated results for the individual state-to-state  $P_{0i}$  reaction probabilities from the entrance channel ground vibrational state of the isolated  $\text{H}_2$  molecule to the exit channel  $i$ -th state. And, also shown are the cumulative reaction probabilities  $N(E) = \sum_{i,j}^{N_{\text{open}}} p_{ij}$ , both obtained from two independent calculations using different sets of calculation parameters, each set corresponding to covering small and large ranges of PES, respectively. The smaller one uses interior basis of  $N_{\text{basis}} = 318$  and the outer



**Figure 3.** Cumulative reaction probabilities  $N(E)$  and individual state-to-state  $P_{0i}$  reaction probabilities obtained from small and large calculations. Large ones with superscript L denoted by assorted lines, and small ones with superscript S by assorted symbols. The isolated  $\text{H}_2$  molecular vibrational states were obtained along the cross section of the two-dimensional PES at the center of  $g(R-p)$ . Subsequently, the threshold energies were calculated around 0.79 eV and 1.27 eV. See text for other detail.



**Figure 4.** Fractional errors in  $N(E)$  and  $P_{0i}$  of small calculation against the corresponding values of large calculation denoted by  $N^e(E)$  and  $P^e_{0i}$ 's, respectively. See text for other detail.

boundary of the scattering coordinate  $R_\alpha$  (and also for  $R_\gamma$ ) is set at 5.7 bohr while the larger one uses interior basis of  $N_{\text{basis}} = 3392$  and the outer boundary is set at 14 bohr. By utilizing the micro-reversibility of the scattering process, we symmetrized reaction probabilities, as  $P_{ij} = \frac{1}{2} (|S_{ij}|^2 + |S_{ji}|^2)$ , before plotting.

The degree of convergence of both results is presented as the fractional errors (i.e., in a form like  $\frac{B-A}{A}$ ) in the results

of the small calculation against those of the larger ones in Figure 4. The errors for all the probabilities are less than 2% for 76 energies among the 101 scattering energies examined while the  $N(E)$  are within 1% error for 84 energies.

Therefore, we could safely concluded that the present approach using a novel volume-Bloch operator is capable of producing sufficiently correct and converged numerical results for reactive scattering even though it is deficient of variationally stable characters.

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