Performance of a fully close-coupled wave packet method for the H_2+LiF(001) model problem

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We have investigated the performance of a fully close-coupled wave packet method and its symmetry-adapted version for a model problem of H_2 scattering from LiF(001). The computational cost of the fully close-coupled methods scales linearly with the number of rotation-diffraction states present in the basis set, provided that the sparseness of the potential coupling matrix is taken into account. For normal incidence, the symmetry adapted version is faster than the conventional close-coupling wave packet method by almost an order of magnitude. An extension of the method to more realistic molecule-surface problems is considered. © *1995 American Institute of Physics.*

I. INTRODUCTION

The wave packet method has become an important tool for performing calculations on molecule-surface scattering. Examples of applications are scattering of molecules from surfaces which contain isolated impurities[1–3] or are otherwise disordered,[2,4,5] phonon-inelastic atom-surface scattering,[2,6] rotationally[2,7–16] or vibrationally[17] inelastic molecule-surface scattering, and reactive molecule-surface scattering.[18–33]

The applicability of wave packet methods to an ever wider range of problems is clearly desirable and, in recent years, much effort has been directed[11,13,32,34–59] at inventing wave packet techniques which are more efficient in terms of either computer time or central memory usage. The numerical efficiency of a wave packet method depends on the number of basis functions used, the spectral range of the Hamiltonian, and the manner in which the matrix-vector products associated with the action of the Hamiltonian on the wave function are carried out.[59,60] Here, we will focus on the matrix-vector products. Depending on the representation of the wave function, improvements in efficiency can be achieved in at least in two ways. This will be illustrated by considering the treatment of the molecular rotations in molecule-corrugated surface scattering as an example.

The first calculations on rotationally inelastic molecule-surface scattering to emerge[7–9] employed a hybrid representation, using a close-coupling, variational basis representation[61] (VBR) for the molecular rotations, and a grid representation for the translational motion of the center of mass. The method thus obtained was called the close-coupled wave packet (CCWP) method. In the "raw" form of the CCWP method, the evaluation of the action of the potential energy operator on the wave function scales with N_{rot}^2, where N_{rot} is the number of rotational states included in the basis set. In a wave packet calculation, most of the computational effort goes into evaluating the action of the Hamiltonian on the wave function through the evaluation of matrix vector products. In the case that many rotational wave functions need to be included in the expansion, most of the computer time is then spent in evaluating potential matrix-vector products. Large increases in efficiency can thus be obtained if the evaluation of the action of the potential energy operator on the wave function is made cheaper.

In considering improvements to the CCWP method, Lemoine and Corey have concentrated their efforts on achieving a higher factorisability of the potential energy operation on the wave function.[13,58,59] This was achieved by changing the representation of the rotational part of the wave function from a variational basis representation to a finite basis representation (FBR). Very generally, an FBR method using the spectral (momentum) representation corresponds to a VBR method in conjunction with the approximation that the potential matrix coupling elements are calculated using an N-point quadrature rule in case N basis functions are used.[61] In a FBR method the spectral basis is chosen such that an efficient and accurate method can be used to transform the wave function from the momentum representation to the coordinate representation and back.[62–64] The most efficient implementation used by Lemoine and Corey for the rotational degrees of freedom employs the spectral representation as the primary representation and has been called the finite basis wave packet (FBWP) method.[58–59] In this implementation, the potential energy operation is performed in the coordinate or discrete variable representation (DVR), and Gauss–Legendre–Fourier transforms are used to switch from the FBR in spherical harmonics to the DVR in θ and ϕ, and back. The Gauss–Legendre–Fourier transforms factorize into two separate matrix-vector multiplications, one of the transformations being block diagonal in the magnetic rotational quantum number. As a result, the potential energy operation on the wave function scales with $N_{\mathrm{rot}}^{3/2}$ rather than with N_{rot}^2, and compared to the conventional CCWP method large increases in efficiency can be obtained for problems requiring a large rotational basis set and involving a molecule-surface potential which is dependent on the azimuthal coordinate ϕ.

It is also possible to increase the efficiency of the CCWP method and stay with the variational basis representation. For a typical molecule-surface problem, the anisotropy of the potential should be small, except maybe at short range. The only spherical harmonics required to describe the long range, C_3 interaction of a homonuclear molecule with a surface are the Y_{00} and Y_{20} harmonics.[65] The frequently used model potential devised by Wolken for the H_2+LiF(001) system only contains these two spherical harmonics.[66] The resulting potential coupling matrix, which is labeled by final and initial rotational states in the CCWP method, is tridiagonal! Once the sparseness of the potential coupling matrix is taken into account, in the CCWP method the potential energy operation scales linearly with N_{rot} rather than quadratically. The size of the prefactor in the scaling relation will depend on just how anisotropic the potential is at short range, which will in turn determine whether the CCWP method or the FBWP method will be more efficient for a given problem.

In this work we investigate to what extent the sparseness of the potential coupling matrix can be used to increase the efficiency of a wave packet method which uses a VBR (Ref. 61) or close-coupling representation. Rather than considering the CCWP method, we take it one step further, using a close-coupled representation also for the diffractive degrees of freedom, as is done in the time-independent close-coupling method.[66] This representation allows one to take maximum advantage of the symmetry relations which exist for normal incidence.[67] While scattering experiments typically do not employ normal incidence, many H_2+metal reaction systems obey "normal energy scaling,"[68–70] meaning that to a good approximation the measured reaction probabilities depend only on the kinetic energy associated with the translational motion normal to the surface. Of course, this dependence can then be obtained from calculations with normal incidence of the wave packet.

For the proposed method to be efficient, it will be necessary that the potential coupling matrix is also sparse in the diffractive degrees of freedom. This is known to be true for potentials constructed from pair interactions,[71,72] and model potentials used in calculations on elastic atom-surface scattering usually employ Fourier terms to order no higher than two.[73–75] Previously, the sparseness of the potential coupling matrix in atom-surface problems has been used in calculations[76] on the He+LiF(001) model system[73] that employed the log derivative version of the Kohn variational principle. The work showed that a very efficient algorithm is obtained if the resulting sparse system of linear equations is solved iteratively. Here, we investigate the influence of the sparseness on the efficiency of a wave packet method employing the fully close-coupled representation for an admittedly simple and favorable case, the Wolken H_2+LiF(001) model problem.[66] Future research will investigate the merits of the proposed method for more realistic potentials.

In Sec. II we summarize the CCWP method and present the new method. We give brief consideration to the model potential used, and discuss the numerical details associated with the calculations. Section III presents and discusses the numerical results of the calculations. Our findings are summarized in Sec. IV.

II. THEORY

A. Outline of wave packet methods

The Hamiltonian describing the dynamics of a rigid rotor, diatomic molecule interacting with a static corrugated surface can be written as

$$\hat{H}=-\frac{1}{2M}\nabla_{\mathbf{R}}^{2}+H_{\text{rot}}+V(X,Y,Z,\theta,\phi). \tag{1}$$

Atomic units were used in Eq. (1). Furthermore, M is the mass of the diatomic molecule, $\mathbf{R}=(X,Y,Z)$ is the position vector of the molecular center of mass, H_{rot} is the Hamiltonian describing the rotational motion of the molecule, and V is the molecule-surface interaction potential which depends on $\mathbf{R}$ and the orientation angles θ and ϕ. The X and Y axes are taken to lie in the plane of the surface along the direction of the lattice vectors (we only consider the case where the surface unit cell is either rectangular or square), Z is taken to be positive above the surface, and θ and ϕ are the polar and azimuthal angles defining the orientation of the molecular axis with respect to Z and X.

Because the Hamiltonian is independent of time, the formal solution to the time-dependent Schrödinger equation can be written as

$$\Psi(\mathbf{R},\theta,\phi,t)=\exp[-i\hat{H}(t-t_0)]\Psi(\mathbf{R},\theta,\phi,t_0), \tag{2}$$

where $\Psi(\mathbf{R},\theta,\phi,t_0)$ represents the initial state of the system. Equation (2) represents an initial value problem. To solve it, we first define an initial wave function

$$\Psi(\mathbf{R},\theta,\phi,t_0)=b(Z)[1/(L_xL_y)]^{1/2}\exp(i\mathbf{K_0}\boldsymbol{\rho})Y_{j_0m_{j0}}(\theta,\phi) \tag{3}$$

which is taken as a Gaussian wave packet in Z

$$b(Z)=[2\pi\xi^2]^{-1/4}\exp[-(Z-Z_0)^2/4\xi^2+ik_{Z_0}Z_0] \tag{4}$$

times the product of a normalized plane wave describing the initial parallel translational motion and a spherical harmonic describing the initial rotational state of the molecule. In Eq. (3), L_x and L_y are the magnitudes of the lattice vectors along X and Y, $\boldsymbol{\rho}=(X,Y)$, and $\mathbf{K}_0$ is the vector of initial parallel momenta (k_{X_0},k_{Y_0}). In Eq. (4), ξ represents the width of the wave packet which is centered on Z_0 and traveling in the Z direction with an average translational momentum k_{Z_0}.

The wave function can then be propagated in time using a numerical algorithm like the Chebychev propagation method[77] or the short iterative Lanczos (SIL) method.[78] Either method involves the repeated evaluation of the action of the Hamiltonian on the wave function. In either method, the upper bound to the size of the timestep that can be used in the propagation is determined by the spectral range W of the Hamiltonian,[60] defined as

$$W=\lambda_{\max}-\lambda_{\min}, \tag{5}$$

where $\lambda_{\max}$ and $\lambda_{\min}$ are the maximum eigenvalues associated with the products of eigenfunctions in which the wave function is expanded. The computational cost of the wave packet propagation depends on the number of basis functions, the spectral range of the Hamiltonian (through the size of the timestep that can be used) and the efficiency with which $\hat{H}\Psi$ is evaluated.[59,60] All of these in turn depend on the method used to expand the wave function, which is discussed in Sec. II B.

The calculation of S-matrix elements involves the projection of the wave function on diffraction-rotation eigenstates. In an elegant method devised by Balint-Kurti *et al.*,[41,45,79] the wave function is analyzed at a fixed value of the scattering coordinate (Z_∞), analogous to what is done in the time-independent close-coupling method.[73] The wave function is projected on rotation-diffraction eigenstates at fixed time intervals, obtaining time-dependent coefficients

$$C_{j'm_j'nm}(Z_\infty,t)=[1/(L_xL_y)]^{1/2}\int_{\boldsymbol{\rho}}\int_{\boldsymbol{\Omega}}\Psi(Z_\infty,\rho,\theta,\phi,t)\times\exp[-i(\mathbf{K_0}+\mathbf{G_{nm}})\rho]\times Y^*_{j'm_j'}(\theta,\phi)d\boldsymbol{\rho}\,d\boldsymbol{\Omega}. \tag{6}$$

In Eq. (6), n and m are the diffraction quantum numbers associated with the final translational state of the molecule, and $\mathbf{G_{nm}}$ is the reciprocal lattice vector given by

$$\mathbf{G_{nm}}=\left(\frac{2\pi n}{L_x},\frac{2\pi m}{L_y}\right). \tag{7}$$

Furthermore, j' and m_j' are the rotational quantum numbers associated with the final rotational state of the molecule. The S-matrix elements $S_{j'm_j'nmj_0m_{j0}}(E)$ for a $(j_0m_{j0}\rightarrow j'm_j'nm)$ transition can be calculated from the $C_{j'm_j'nm}(Z_\infty,t)$ using time-energy Fourier transforms as outlined in Refs. 41, 45, and 79. The probabilities $P(j_0m_{j0}\rightarrow j'm_j'nm)$ are related to these S-matrix elements through

$$P(j_0m_{j0}\rightarrow j'm_j'nm)=|S_{j'm_j'nmj_0m_{j0}}(E)|^2. \tag{8}$$

A nice feature of the asymptotic analysis method discussed earlier is that the scattered wave function is not needed beyond the analysis value of the scattering coordinate Z_∞. Methods which share this feature and also rely on time-to-energy Fourier transforms are methods due to Hoffman *et al.*[80] and Neuhauser *et al.*[81] In the method of Hoffman *et al.*,[80] T-matrix elements are obtained using time-to-energy transforms of the time-dependent amplitude density, which is nonzero only over the range of the potential. Because this scheme uses the amplitude density, it is best used in conjunction with a time-dependent integral equations approach. Neuhauser's method[81] also involves time-to-energy Fourier transforms and analysis of the wave function at a particular value of the scattering (reaction) coordinate. It involves the calculation of fluxes through the surface defined by the analysis value of the scattering (reaction) coordinate, and is in a sense more general in that it can also be used to calculate probabilities which are resolved with respect to one quantum number and averaged over another.

Because the scattered wave function is not needed beyond Z_∞, the grid in the scattering coordinate needs to contain only the range over which the potential is nonzero plus a small interval used to absorb the scattered wave packet and lying beyond Z_∞. To absorb the outgoing wave packet, we add an optical potential of the quadratic form[82]

$$V_I(Z)=-iA_2(\tfrac{3}{2}\bar{Z}^2), \tag{9a}$$

$$\bar{Z}=(Z-Z_I^{\min})/L, \tag{9b}$$

to the Hamiltonian of Eq. (1), the optical potential being defined over the range $[Z_I^{\min},Z_I^{\min}+L]$.

B. Description of individual wave packet methods

1. The CCWP method

In the CCWP method,[7–9,14] the wave function is written as an expansion in a set of rotational basis functions and represented on a rectangular grid of regularly spaced points in X, Y, and Z:

$$\Psi(t)=\sum_{jm_j}\chi^{j_0m_{j0}}_{jm_j}(\mathbf{R},t)Y_{jm_j}(\theta,\phi). \tag{10}$$

Along Z, Y, and X, N_z, N_y and N_x regularly spaced grid points are used. For a square lattice, a square grid of points in X and Y is used ($N_y=N_x$). In the rotational expansion, N_{rot} rotational states are included, j ranging from 0 to $j_{\max}$.

Using the expansion of Eq. (10), the action of the kinetic energy operator associated with the translational motion of the molecule can be efficiently evaluated using consecutive FFT's (Refs. 62 and 63) of the $\chi^{j_0m_{j0}}_{jm_j}(\mathbf{R},t)$ along Z, Y, and X. The associated computational cost scales as $N_zN_{xy}N_{\text{rot}}\times(\log N_z+\log N_y+\log N_x)$, where N_{xy} is the product of N_y and N_x. The actual kinetic energy operation is performed in momentum space by performing simple multiplications, which scale as $N_zN_{xy}N_{\text{rot}}$. Because the expansion is in rotational eigenfunctions, the evaluation of the rotational energy operator simply involves the multiplication of each $\chi^{j_0m_{j0}}_{jm_j}(\mathbf{R},t)$ with $B_0j(j+1)$ on each grid point, scaling as $N_zN_{xy}N_{\text{rot}}$ (B_0 is the rotational constant of the molecule). A similar scaling is obtained for the multiplication with the optical potential, except that this operation is only performed for a limited number of points in Z.

The potential energy operation is performed by premultiplying the vector $\chi^{j_0m_{j0}}_{jm_j}(\mathbf{R},t)$ with the potential coupling matrix on each point (Z,Y,X). The elements of the matrix are given by

$$V_{j'm_j'jm_j}(\mathbf{R})=\int Y^*_{jm_j'}(\theta,\phi)V(\mathbf{R},\theta,\phi)Y_{jm_j}(\theta,\phi)d\boldsymbol{\Omega}. \tag{11}$$

If no attention is paid to the possible sparseness of the matrix, the potential energy operation scales as $N_zN_{xy}N^2_{\text{rot}}$. If, on the other hand, the potential coupling matrix is sparse an upper bound to the scaling is given by $N_zN_{xy}N_{\text{rot}}N^{\text{rot}}_{\text{coup}}$, where $N^{\text{rot}}_{\text{coup}}$ is the maximum number of rotational states the potential can couple with a given initial state on any point (X,Y,Z). In the case of a homonuclear diatomic molecule interacting with a surface through a potential containing no azimuthal dependence, $N^{\text{rot}}_{\text{coup}}$ is equal to $j_V^{\max}+1$, where $j_V^{\max}$ is the maximum order of the spherical harmonics Y_{j0} occurring in the expansion of the potential.

TABLE I. Scaling of the operations used in evaluating the Hamiltonian and propagating the wave function. We have omitted a common factor of N_z in all the scale factors collected in the table, and $M_{xy}=\log N_x+\log N_y$.

Operation	CCWP	RDWP	SAWP
Propagation	$N_{xy}N_{\rm rot}$	$N_{\rm dif}N_{\rm rot}$	$N_{\rm dif}^{a1}N_{\rm rot}$
V_I	$N_{xy}N_{\rm rot}$	$N_{\rm dif}N_{\rm rot}$	$N_{\rm dif}^{a1}N_{\rm rot}$
K, multiplications	$N_{xy}N_{\rm rot}$	$N_{\rm dif}N_{\rm rot}$	$N_{\rm dif}^{a1}N_{\rm rot}$
K_z, FFT's	$N_{xy}N_{\rm rot}\log N_z$	$N_{\rm dif}N_{\rm rot}\log N_z$	$N_{\rm dif}^{a1}N_{\rm rot}\log N_z$
$K_{\rm dif}$, FFT's	$N_{xy}N_{\rm rot}M_{xy}$		
Potential	$N_{xy}N_{\rm rot}N_{\rm coup}^{\rm rot}$	$N_{\rm dif}N_{\rm rot}N_{\rm coup}^{\rm rot}N_{\rm coup}^{\rm dif}$	$N_{\rm dif}^{a1}N_{\rm rot}N_{\rm coup}^{\rm rot}N_{\rm coup}^{\rm dif}$

TABLE II. The memory required to store the wave function using the Chebychev propagation method (C) and the SIL method of order 9 (L) is given for the different wave packet methods discussed in Sec. II B. Also given is the amount of memory required to store the potential coupling matrix for a potential which does not depend on the azimuthal angle ϕ. A common factor of $N_z\times N_{\rm rot}$ has been omitted in all cases.

Storage for:	CCWP	RDWP	SAWP
Wave function (C)	$8\times N_{xy}$	$8\times N_{\rm dif}$	$8\times N_{\rm dif}^{a1}$
Wave function (L)	$20\times N_{xy}$	$20\times N_{\rm dif}$	$20\times N_{\rm dif}^{a1}$
Potential	$N_{xy}\times N_{\rm coup}^{\rm rot}$	$N_{\rm dif}\times N_{\rm coup}^{\rm rot}\times N_{\rm coup}^{\rm dif}$	$N_{\rm dif}^{a1}\times N_{\rm coup}^{\rm rot}\times N_{\rm coup}^{\rm dif}$

Taking the sparseness of the potential into account thus leads to a scaling of the potential energy operation which is linear with $N_{\rm rot}$, the prefactor being dependent on how many spherical harmonics need to be used in the potential expansion. A modified CCWP method which takes sparseness into account should then scale especially favorable for systems requiring a large rotational basis set (due to a small rotational constant) while possessing little anisotropy in the molecule-surface interaction potential.

The propagation of the wave function involves additions and (in the case of the SIL propagator[78]) the calculation of overlap integrals which all scale as $N_zN_{xy}N_{\rm rot}$. The scaling of the operations involved in propagating the wave function in time using the CCWP method are summarized in Table I.

In the CCWP method, the calculation of the initial wave function [Eqs. (3) and (4)] can be performed trivially by calculating $b(Z)x\exp[i\mathbf{K_0}\rho]$ on the grid in X, Y, and Z. Arbitrary angles of incidence can be handled by extending the FFT scheme using the shifting theorem of Fourier analysis, as described in Ref. 54. The extra (shifting) operations required scale as $N_zN_{xy}N_{\rm rot}$. In performing the asymptotic analysis, the projection of the wave function on the rotation-diffraction eigenstates can be done using consecutive FFT's of $\chi_{jm_j}^{j_0m_{j0}}(Z_\infty,Y,X,t)$ along Y and X for all rotational states present in the basis set [see Eq. (6)]. The associated computational cost is negligibly small when compared to the cost of evaluating the action of the Hamiltonian on the wave function.

The amount of central memory required in the CCWP method depends on which propagation method is used. The Chebychev algorithm[77] requires four storage arrays,[83] where the memory taken up by one storage array is the amount of memory required to hold the full wave function. The SIL method[78] of order $N_{\rm lan}$ requires $(N_{\rm lan}+1)$ storage arrays.[83] In the CCWP method, the memory required to store the wave function is $2\times N_zN_{xy}N_{\rm rot}$ (the factor 2 is from the wave function being complex). If the sparseness of the potential coupling matrix is used, an upper bound to the memory required to store this matrix is $N_zN_{xy}N_{\rm rot}N_{\rm coup}^{\rm rot}$ in case the potential shows no azimuthal dependence (the coupling matrix being real symmetric), otherwise it is $2\times N_zN_{xy}N_{\rm rot}N_{\rm coup}^{\rm rot}$ (the factor 2 arises from the coupling matrix being complex Hermitian). The memory requirements of the CCWP method are summarized in Table II.

2. The rotationally and diffractionally close-coupled wave packet method

It is also possible to expand the wave function on a grid in Z and in rotation-diffraction eigenfunctions as is done in the time-independent close-coupling method.[73] The expansion is

$$\Psi(t)=\sum_{jm_jnm} f_{jm_jnm}^{j_0m_{j0}}(Z,t)[1/(L_xL_y)]^{1/2} \times\exp[i(\mathbf{K_0}+\mathbf{G_{nm}})\boldsymbol{\rho}]Y_{jm_j}(\theta,\phi). \qquad (12)$$

We will call the resulting method the rotationally and diffractionally close-coupled wave packet (RDWP) method.

In the RDWP method, N_z points are used for the dependence of the wave function on Z, and $N_{\rm rot}$ rotational states are included in the rotational basis set, j ranging from 0 to $j_{\rm max}$. One advantage of the RDWP method over the CCWP method is that there is an enhanced freedom in the choice of diffraction eigenstates to expand in. The spectral diffraction basis which is effectively used in the CCWP method is a square grid of N_{xy} points in the two-dimensional (p_x,p_y) momentum space. In calculations employing the close-coupling method often good results can be obtained by including diffraction states up to diffraction order $M_{\rm dif}$, where the diffraction order$=|n|+|m|$. The resulting spectral ''grid'' is ''diamond shaped'' in momentum space, containing $N_{\rm dif}=M_{\rm dif}^2+(M_{\rm dif}+1)^2$ diffraction eigenstates. In previous work[54] on scattering from a surface possessing C_{4v} symmetry, which compared results of CCWP calculations with results of (time-independent) close-coupling (CC) calculations, we found the number of diffraction states needed to get convergence employing a diamond shaped (in momentum space) grid to be much less (61, $M_{\rm dif}=5$) than the number of diffraction states effectively required for convergence in a CCWP calculation (100, $N_x=N_y=10$).

Using the expansion of Eq. (12), the action of the kinetic energy operator associated with the translational motion of the molecule along Z can be evaluated using FFT's along Z for each rotation-diffraction eigenstate. The computational effort involved scales as $N_zN_{\rm dif}N_{\rm rot}\log N_z$ rather than as $N_zN_{xy}N_{\rm rot}\log N_z$ as is the case in the CCWP method. This will usually give some enhancement of efficiency because, as explained above, the number of diffraction states $N_{\rm dif}$ required to obtain converged results will usually be less than N_{xy}. More importantly, an additional advantage of the RDWP method over the CCWP method is that the FFT's along Y and X can now be avoided in the evaluation of the Laplacian operator, because the wave function is already expanded in diffraction eigenfunctions. In the RDWP method, the potential energy operation is performed by premultiplying the vector $f^{j_0m_{j0}}_{jm_jnm}(Z,t)$ with the rotation-diffraction potential coupling matrix on each point in Z. The elements of the matrix are given by

$$\begin{aligned}&V_{j'm_j'n'm'jm_jnm}(Z)\\ &\quad=1/(L_xL_y)\int Y^*_{jm_j'}(\theta,\phi)\exp[-i(\mathbf{K_0}+\mathbf{G_{n'm'}})\boldsymbol{\rho}]\\ &\qquad\times V(\mathbf{R},\theta,\phi)\exp[i(\mathbf{K_0}+\mathbf{G_{nm}})\boldsymbol{\rho}]\\ &\qquad\times Y_{jm_j}(\theta,\phi)d\boldsymbol{\rho}\,d\boldsymbol{\Omega}.\end{aligned}\tag{13}$$

If no advantage is taken of the sparseness of the potential coupling matrix, the potential energy operation will scale as $N_zN_{\rm dif}^2N_{\rm rot}^2$, which would be very unfavorable. On the other hand, the computational cost will scale no worse than $N_zN_{\rm dif}N_{\rm rot}N_{\rm coup}^{\rm rot}N_{\rm coup}^{\rm dif}$ if the sparseness of the potential coupling matrix is taken into account, where $N_{\rm coup}^{\rm dif}$ is the maximum number of diffraction states to which the potential will couple a given rotation-diffraction state (the rotational state of the coupled states being the same). Comparing this to the cost of the potential energy operation in the CCWP method (see Table I), we find that in the RDWP method we should expect the potential energy operation to be more expensive by a factor of $N_{\rm dif}/N_{xy}\times N_{\rm coup}^{\rm dif}$. An approximate realistic value of $N_{\rm dif}/N_{xy}$ is 0.6 (see preceding text and Sec. II F), and $N_{\rm coup}^{\rm dif}$ is 5 in case the potential contains Fourier terms of order up to 1, which means that for such a potential we should expect the potential energy operator evaluation to become more expensive by a factor of 3. Whether the RDWP method will be more efficient than the CCWP method will then depend on to what extent the loss in efficiency in performing the potential energy operation is offset by gains in efficiency in evaluating the action of the kinetic energy operator. The scaling behavior of the other operations required to propagate the wave function in time are summarized in Table I.

In the RDWP method, the calculation of the initial wave function [Eqs. (3) and (4)] is even more trivial than in the CCWP method, and simply involves setting $f^{j_0m_{j0}}_{j_0m_{j0}00}(Z,t_0)$ equal to $b(Z)$. Arbitrary angles of incidence can be handled just as easily as in the CC method. In the RDWP method, the asymptotic analysis is even more easy than in the CCWP method, and simply involves setting $C_{jm_jnm}(Z_\infty,t)$ equal to $f^{j_0m_{j0}}_{jm_jnm}(Z_\infty,t)$.

An advantage of any method doing a full expansion in molecular eigenstate channels is that, if the collision energy distribution is not too broad, the energy of the translational motion in the scattering coordinate will be reasonably well defined for a given scattered channel. This makes it possible to use an optimal procedure to absorb the scattered wave function, by making the optical potential channel dependent. In practical calculations, one will typically assign a fixed value to L, the range over which the optical potential acts, enabling one to work with a grid of fixed size. The proportionality constant of the optical potential [A_2 for a quadratic potential, see Eq. (9a)] can then be adjusted to the translational energy with which the scattered channel is expected to emerge, using procedures described in Ref. 82.

In the RDWP method, the amount of memory required to store the wave function is $2\times N_zN_{\rm dif}N_{\rm rot}$. If the sparseness of the potential coupling matrix is used, an upper bound to the memory required to store this matrix is $N_zN_{\rm dif}N_{\rm rot}N_{\rm coup}^{\rm rot}N_{\rm coup}^{\rm dif}$ in case the potential shows no azimuthal dependence, otherwise it is $2\times N_zN_{\rm dif}N_{\rm rot}N_{\rm coup}^{\rm rot}N_{\rm coup}^{\rm dif}$. Compared to the CCWP method (see Table II), we find that usually less memory will be required to store the wave function (we will typically have $N_{\rm dif}<N_{xy}$) while more memory will be required to store the potential coupling matrix ($N_{\rm dif}N_{\rm coup}^{\rm dif}>N_{xy}$).

3. The symmetry adapted rotationally and diffractionally close-coupled wave packet method

In the case that the molecule is incident along a symmetry direction of the crystal,[84,85] and especially in the case of normal incidence,[67] a much more efficient method than the RDWP method is obtained if the wave function is expanded in symmetry adapted diffraction-rotation eigenfunctions. We will call the method thus obtained the symmetry adapted rotationally and diffractionally close-coupled wave packet (SAWP) method. Here, we limit ourselves to a discussion of the case of normal incidence on a crystal surface which has C_{4v} point group symmetry, as is the case for the LiF(001) surface, with the molecule-surface potential being independent of the azimuthal angle ϕ. Extensions to ϕ-dependent molecule-surface potentials and incidence along a symmetry direction will be made in future work.

In the case of normal incidence and a ϕ-independent molecule-surface potential, we need to include only parallel translational eigenfunctions which are totally symmetric under C_{4v} symmetry.[67] The resulting expansion is

$$\Psi(t)=\sum_{jnm} g^{j_0m_{j0}}_{jm_{j0}nm}(Z,t)H_{nm}(\boldsymbol{\rho})Y_{jm_{j0}}(\theta,\phi),\quad n\geqslant m\geqslant 0\tag{14}$$

and the symmetry adapted eigenfunctions are given by[67]

$$\begin{aligned}H_{nm}(\boldsymbol{\rho})=&(\tfrac{1}{8})^{1/2}[1/(L_xL_y)]^{1/2}[G_{nm}(\boldsymbol{\rho})\\ &+G_{n-m}(\boldsymbol{\rho})+G_{-n-m}(\boldsymbol{\rho})+G_{-nm}(\boldsymbol{\rho})\\ &+G_{mn}(\boldsymbol{\rho})+G_{m-n}(\boldsymbol{\rho})+G_{-m-n}(\boldsymbol{\rho})\\ &+G_{-mn}(\boldsymbol{\rho})],\quad n>m>0\end{aligned}\tag{15a}$$

$$\begin{aligned}H_{nm}(\boldsymbol{\rho})=&\tfrac{1}{2}[1/(L_xL_y)]^{1/2}[G_{nm}(\boldsymbol{\rho})\\ &+G_{-nm}(\boldsymbol{\rho})+G_{mn}(\boldsymbol{\rho})\\ &+G_{m-n}(\boldsymbol{\rho})],\quad n>m=0\end{aligned}\tag{15b}$$

$$\begin{aligned}H_{nm}(\boldsymbol{\rho})=&\tfrac{1}{2}[1/(L_xL_y)]^{1/2}[G_{nm}(\boldsymbol{\rho})\\ &+G_{n-m}(\boldsymbol{\rho})+G_{-m-n}(\boldsymbol{\rho})\\ &+G_{-mn}(\boldsymbol{\rho})],\quad n=m>0\end{aligned}\tag{15c}$$

$$H_{nm}(\boldsymbol{\rho})=[1/(L_xL_y)]^{1/2}, \quad n=m=0 \tag{15d}$$

where

$$G_{nm}(\boldsymbol{\rho})=\exp(i\mathbf{G_{nm}}\boldsymbol{\rho}). \tag{15e}$$

For the case of a molecule-surface potential showing no dependence on the azimuthal angle ϕ, the scaling relations found for the RDWP method are also valid for the SAWP method, except that now we can replace N_{dif} by the number of totally symmetric parallel translational eigenstates, N_{dif}^{a1} (see also Table I). Considering once more the diamond-shaped grid of momentum eigenstates discussed in considering the RDWP method, N_{dif}^{a1} is the number of momentum eigenstates contained in a triangle which is obtained by intersecting the "diamond" with a line that makes a positive angle of 45° with the p_x axis and passes through the origin of the two-dimensional (p_x,p_y) space. The number N_{dif}^{a1} for such a "triangular" grid is $(M_{\text{dif}}+1)(M_{\text{dif}}+3)/4$ for odd maximum diffraction order M_{dif}, and $(M_{\text{dif}}+2)^2/4$ for even maximum diffraction order M_{dif}. For selected values of M_{dif} we give the values of N_{dif}^{a1},N_{dif} and the expected gain in efficiency $N_{\text{dif}}/N_{\text{dif}}^{a1}$ if symmetry is used in the SAWP method in Table III.

As can be seen from Table III, the expected gain in efficiency obtained by using symmetry only slowly approaches the upper bound of 8. In practical situations, in case of normal incidence one will have to be satisfied with gains of the order of 5 or 6 when using symmetry. Nevertheless, when considering the computational cost of performing the potential energy operation on the wave function using the example previously discussed ($M_{\text{dif}}=5$, $N_x=N_y=10$, Fourier terms present in the potential up to order 1) we now find that the SAWP method should be cheaper than the nonsymmetry adapted CCWP method even for this operation ($N_{\text{dif}}^{a1}/N_{xy} \times N_{\text{coup}}^{\text{dif}} = 0.6$, see Tables I and II).

In the SAWP method, the calculation of the initial wave function [Eqs. (3) and (4)] is just as easy as in the RDWP method, and simply involves setting $g_{j_0m_{j0}00}^{j_0m_{j0}}(Z,t_0)$ equal to $b(Z)$. The asymptotic analysis is also performed analogously, and involves setting $C_{jm_{j0}nm}(Z_\infty,t)$ equal to $g_{jm_{j0}nm}^{j_0m_{j0}}(Z_\infty,t)$. The coefficients are calculated for $n \geqslant m \geqslant 0$ only. From these coefficients, S-matrix elements also labeled by the symmetry index A_1 are calculated for the same values of n and m. The actual S-matrix elements for arbitrary n, m can then be obtained from

$$S_{j'm_{j0}nmj_0m_{j0}}(E)=S_{j'm_{j0}mnj_0m_{j0}}(E)$$

$$=\sqrt{\tfrac{1}{8}}\,S_{A_1j'm_{j0}|n||m|j_0m_{j0}}(E), \quad |n|>|m|>0 \tag{16a}$$

$$S_{j'm_{j0}nmj_0m_{j0}}(E)$$

$$=S_{j'm_{j0}mnj_0m_{j0}}(E)=\tfrac{1}{2}\,S_{A_1j'm_{j0}|n||m|j_0m_{j0}}(E),$$

$$|n|>|m|=0 \;\text{ or }\; |n|=|m| \tag{16b}$$

$$S_{j'm_{j0}00j_0m_{j0}}(E)=S_{A_1j'm_j'00j_0m_{j0}}(E). \tag{16c}$$

TABLE III. For selected values of the maximum diffraction order M_{dif} of diffraction states included in the basis set, we give the values of N_{dif}^{a1}, N_{dif} and the expected gain in efficiency (compared to the RDWP method) $N_{\text{dif}}/N_{\text{dif}}^{a1}$ when symmetry is used in the SAWP method. For the meaning of the parameters N_{dif}^{a1} and N_{dif}, see the text.

M_{dif}	N_{dif}^{a1}	N_{dif}	Gain
1	2	5	2.50
2	4	13	3.25
3	6	25	4.17
4	9	41	4.55
5	12	61	5.08
6	16	85	5.31
8	25	145	5.80
10	36	221	6.14
15	72	481	6.68
25	182	1301	7.15
100	2601	20201	7.77

The amount of memory required in the SAWP method can be obtained from that required by the RDWP method by substituting N_{dif}^{a1} for N_{dif} in all the expressions given in Table II. Comparing to the CCWP method (see Table II), we find that much less memory will be required to store the wave function. We expect that the amount of memory required to store the potential coupling matrix will usually not be very different for the SAWP and CCWP methods ($N_{\text{dif}}^{a1}N_{\text{coup}}^{\text{dif}} \approx N_{xy}$).

4. A symmetry adapted close-coupling wave packet method

Another approach to the use of point group symmetry in molecule-surface scattering was recently considered by Lemoine.[57] The approach is to retain the minimum number of symmetry-needed diffraction states rather than set up a basis of symmetry-adapted states. In the method thus obtained, the action of the potential energy operator is evaluated in the coordinate representation. For normal incidence the diffractive kinetic energy can be evaluated using fast cosine transforms (FCT's) along X and Y, or using a symmetry adapted DVR method. In the case that few diffractive states are required, the latter scheme will usually be more efficient, because the FCT scheme cannot take full advantage of the symmetry relations arising from normal incidence for C_{4v} symmetry of the surface.[57]

The scheme discussed by Lemoine can be easily extended to rotationally inelastic molecule-surface scattering. Actually, Lemoine has already used it in calculations on scattering of N_2 using the finite basis representation method for the molecular rotations.[59] We will call the method that would be obtained if the close-coupling representation (VBR) for the rotational states would be retained the symmetry adapted CCWP method, and abbreviate it as SNWP method, to emphasize that symmetry needed rather than symmetry adapted states are used in the basis set. In this work, we do not present any numerical results of the SNWP method, though estimates of its computational cost will be given in Sec. III. However, we will discuss the scaling relations for this method briefly here.

Because a grid representation is retained for the diffractive degrees of freedom, the number of rotation-diffraction states effectively present in the basis set will be $N_{xy}^{a1}N_{\mathrm{rot}}$ rather than $N_{\mathrm{dif}}^{a1}N_{\mathrm{rot}}$. Here, N_{xy}^{a1} is the number of momentum states contained within the triangle that is obtained by intersecting the square containing the momentum eigenstates and the p_x axis by a line making a positive angle of 45° with this axis and passing through the origin. For $N_x=N_y=10$, $N_{xy}^{a1}=21$ is obtained, which is considerably more than the value of $N_{\mathrm{dif}}^{a1}(12)$ obtained for $M_{\mathrm{dif}}=5$. The scaling relations of the SNWP method for the propagation of the wave function, the multiplications with the optical potential and the kinetic energy for motion along Z, and the FFT's along Z can then be obtained from those of the SAWP method by substituting N_{xy}^{a1} for N_{dif}^{a1} in the expressions given in Table I. The evaluation of the diffractive kinetic energy should scale approximately as $1/5\times N_{xy}^{2}$ in case a symmetry adapted DVR method is used (the factor 1/5 is from 21/100 for $N_x=N_y$). As was discussed before, the calculation of the diffractive energy in the SAWP method is much cheaper because it does not require any transformations.

While the SNWP method should be less efficient than the SAWP method for all the operations discussed above, it should be more efficient in performing the potential energy operation, which scales as $N_{xy}^{a1}N_{\mathrm{rot}}N_{\mathrm{coup}}^{\mathrm{rot}}$ in the SNWP method. Thus, in evaluating the action of the potential energy operator the SNWP method will be more effective than the SAWP method by a factor $N_{\mathrm{dif}}^{a1}/N_{xy}^{a1}\times N_{\mathrm{coup}}^{\mathrm{dif}}$. For the example we have been discussing so far ($N_{\mathrm{coup}}^{\mathrm{dif}}=5$) the gain in efficiency is a factor of 2.86. As will be seen in Sec. III, where we compare estimated costs of using the SNWP method with the actual cost of the SAWP method, for the example discussed in Sec. III this gain is more than offset by the losses in efficiency occurred for the other operations. To what extent this will hold for other molecule-surface problems will depend on the extent of corrugation of the surface (this determines the value of $N_{\mathrm{coup}}^{\mathrm{dif}}$) but also on the anisotropy of the molecule-surface potential (this determines the value of $N_{\mathrm{coup}}^{\mathrm{rot}}$). The degree of anisotropy of the potential will determine how expensive the potential energy operation is relative to the diffractive kinetic energy operation. The more expensive the potential energy operation will be relative to the diffractive kinetic energy operation, the more efficient the SNWP method will be compared to the SAWP method.

The amount of memory required by the SNWP method can be obtained by that required for the CCWP method by substituting N_{xy}^{a1} for N_{xy} in all expressions given in Table II. We expect that in terms of memory usage the SNWP method will generally the most efficient method, especially in the case that the Chebychev propagator is used.

C. The spectral range associated with the different methods

The amount of Hamiltonian operations which are required to propagate the wave function over some given time Δt is linearly proportional to the spectral range of the Hamiltonian for all propagation methods.[60] In a wave packet calculation, the spectral range can be calculated using

$$\lambda_{\mathrm{max}}=T_{\mathrm{max}}^{z}+T_{\mathrm{max}}^{y}+T_{\mathrm{max}}^{x}+T_{\mathrm{max}}^{\mathrm{rot}}+V_{\mathrm{max}}, \tag{17a}$$

$$\lambda_{\mathrm{max}}=V_{\mathrm{min}}, \tag{17b}$$

in Eq. (5). In Eq. (17a), the maximum kinetic energies for translational motion along a particular direction can be straightforwardly calculated from the grid spacing along that direction. The calculation of the maximum rotational kinetic energy is likewise straightforward. However, as discussed later the calculation of the maximum potential energy on the grid is not so straightforward if the potential energy operation is not performed in the coordinate representation.
In a VBR method, one can approximate V_{max} by the spectral radius $\rho(V)$, which is the largest eigen value of the potential coupling matrix. An upper bound to the spectral radius is given by[9]

$$\rho(V)=\leq \max_i \sum_j |V_{ij}|. \tag{18}$$

In the CCWP or SNWP method, $\rho(V)$ would be calculated for all points (X,Y,Z) and the maximum value would be used for V_{max}. In the RDWP and SAWP method, $\rho(V)$ is calculated for all the grid values of Z, and the maximum taken. Because in all cases an upper bound estimate would be used to calculate V_{max}, one would typically use a timestep that would be smaller than necessary.

It is a long standing practice to impose a maximum on the potential energy in order to reduce the spectral range. It is likewise useful to impose a maximum on the total kinetic energy.[59,86] Imposing a maximum T_{cut} on the total kinetic energy is straightforward in the CCWP, RDWP, and SAWP methods. In the RDWP and SAWP methods, the wave function is first transformed from the coordinate representation in Z to the momentum representation in Z. In the CCWP method, the same is done, also transforming along X and Y. Once the wave function is obtained in the fully spectral representation, is is multiplied with the total kinetic energy on each "grid point" in momentum space, taken into account the imposed cutoff value T_{cut}. Imposing T_{cut} in the SNWP scheme is likewise easy if FCT's are employed in the calculation of the diffractive kinetic energy. However, it should be noted that if one wants to impose a cutoff value on the total kinetic energy the use of the symmetry adapted DVR method to transform from the X,Y coordinate space to momentum space becomes less favorable, because two DVR transformations have to be performed rather than one matrix-vector multiplication which includes both the transformations and the multiplication with the kinetic energy in momentum space.

A great advantage of a FBR method like the FBWP method[58,59] is that in this method it is also easy to impose a maximum on the potential energy operator, since the potential energy operation is performed in the coordinate representation. This advantage is not shared by methods employing the close-coupling representation or VBR. What one can do is use a procedure that ensures that the potential is not changed if its value is less than the maximum V_{max}^{co} that would be imposed in case the potential energy operation would be performed in the coordinate representation. This can be ensured by expanding the molecule-surface potential in symmetry adapted functions that are normalized in such a way that their maximum absolute value is 1, i.e.,

$$V(Z,Y,X,\theta,\phi)=\sum_{j\geqslant 0} C_j(Z,Y,X)V_j(\theta,\phi) \tag{19a}$$

or

$$V(Z,Y,X,\theta,\phi)=\sum_{j\geqslant 0} C_j(Z)V_j(X,Y,\theta,\phi). \tag{19b}$$

In Eqs. (19), V_0 will always be $\sqrt{2\pi}Y_{00}$ for all methods discussed in Sec. II B. One then calculates

$$V_{\max}^{\text{cut}}=V_{\max}^{\text{co}}C_V, \tag{20a}$$

$$C_V=\max_{\text{grid}}\left(1+\sum_{j\geqslant 1}|C_j|/C_0\right), \tag{20b}$$

considering grid points close to the surface.

Next, before calculating the potential coupling matrix, in all cases where we find that $C_0>V_{\max}^{\text{cut}}$, we impose a cutoff on the potential energy expansion by setting

$$C_0=V_{\max}^{\text{cut}}, \tag{21a}$$

$$C_j=0, \quad j\geqslant 1. \tag{21b}$$

A safe estimate of $V_{\max}$ is then obtained by setting it to the square of $V_{\max}^{\text{cut}}$. In the case of a weakly anisotropic potential like the example considered in Sec. II E, we will typically have $V_{\max}^{\text{cut}} \approx 1.4 \times V_{\max}^{co}$, so that the calculated $V_{\max}$ will be twice the one that would be used in a FBR method. Assuming the minimum value of the potential to be small, if we use the same cutoff value for the total kinetic energy as the value we would use for $V_{\max}$ in an FBR calculation, the spectral range associated with a method employing the VBR or close coupling representation is roughly 1.5 that of a method employing the FBR.

D. Initial wave packet propagation

In a wave packet calculation, the grid in the scattering coordinate can be made smaller if a separate grid (we call this grid the elastic grid) which extends to larger values of Z is used to bring in the initial wave function.[38] This technique was used in all the methods discussed in Sec. II B. The elastic grid is used to hold the diffractionally and rotationally elastic channel defined by $h(Z)$, until this channel can be accommodated on the part of the ‘‘regular’’ grid not affected by the optical potential, which does not act on the ‘‘elastic’’ grid. In practice, we check whether the value of the norm of the wave packet, as calculated over the range of Z starting with $Z_I^{\min}$ (where the optical potential starts to act, see Sec. II A) becomes less than some tolerance parameter tol_{sp}, or whether this norm starts increasing again. Once this is the case, the wave function is transferred to the regular grid and propagation continues on this grid only.

In the initial propagation on both the regular grid and the elastic grid, the kinetic energy operation is performed separately on each grid. To evaluate the action of the potential energy operator in the range of the scattering coordinate where the potential energy is not zero, the elastic part of the wave function is first transferred to the regular grid. This is a trivial operation if the RDWP or SAWP method is used. If the CCWP method is used, at each point in Z contained in the regular grid it involves a multiplication of $h(Z)$ with $[1/(L_xL_y)]^{1/2}\exp(i\mathbf{K_0}\rho)$ to obtain the wave function on the grid points in X and Y. Next, the potential energy operation is performed on the regular grid. The resulting elastic part of the wave function is then transferred back to the elastic grid, which is once again a rather trivial operation in the RDWP and SAWP methods. In the CCWP method, the new value of the elastic wave function $h'(Z)$ is first calculated from

$$h'(Z)=\int_{\boldsymbol{\rho}}[1/(L_xL_y)]^{1/2}\ \exp(-i\mathbf{K_0}\boldsymbol{\rho})\chi_{j_0m_{j0}}^{j_0m_{j0}}(\mathbf{R},t)\,d\boldsymbol{\rho}. \tag{22}$$

The transfer of the elastic part from the regular grid to the elastic grid is then completed by subtracting $h'(Z) \times \sqrt{1/(L_xL_y)}\ \exp(i\mathbf{K_0}\rho)$ from $\chi_{j_0m_{j0}}^{j_0m_{j0}}(\mathbf{R},t)$, thus projecting out the elastic part of the wave function.

The method of bringing in the elastic part of the wave function on a separate grid is easy to apply and, in favorable cases, may save up to a factor of 2 of computer time. Another method to reduce the grid size is the use of a floating grid, the range of which can be adjusted to contain the wave packet as it moves in time.[11] This method may allow for even larger reductions in computer time in favorable cases[11] (high collision energy, little energy transfer to the rotational and diffractive degrees of freedom, no trapping), but is more difficult to implement.

E. Model potential

The model potential we use in this work is that devised by Wolken[66] for H_2+LiF(001). It can be written as

$$V(X,Y,Z,\theta)=V(X,Y,Z)\times V_2(\theta), \tag{23a}$$

where

$$V_2(\theta)=1+\lambda P_2(\cos\ \theta), \tag{23b}$$

$$V(X,Y,Z)=V_0(Z)+V_1(Z)Q(X,Y), \tag{23c}$$

$$V_0(Z)=D\ \exp[\alpha(Z_{V0}-Z)]\times\{\exp[\alpha(Z_{V0}-Z)]-2\}, \tag{23d}$$

$$V_1(Z)=-2\beta D\ \exp[2\alpha(Z_{V0}-Z)], \tag{23e}$$

$$Q(X,Y)=\cos(2\pi X/a)+\cos(2\pi Y/a). \tag{23f}$$

The parameters used in this study are the parameters a=2.84 Å, α=1.18 Å^{-1}, D=38 meV, and λ=0.24 also used by Wolken, while for the corrugation parameter β we use 0.03. The choice of the parameter Z_{V0} is arbitrary, and we set it to 5 bohr. The parameter a is simply the LiF(001) lattice constant.

The Wolken potential [Eq. (23)] contains no dependence on the azimuthal angle of orientation ϕ. The maximum value of j in the potential expansion $j_V^{\max}$ is 2 and, therefore, we have $N_{\text{coup}}^{\text{rot}}$=3. In the potential expansion, Fourier terms are present up to order 1 [through the symmetry adapted func-

TABLE IV. Numerical parameters used as input in the calculations are given.

parameter	CCWP	RDWP	SAWP
Initial wave packet			
Width ξ (bohrs)	1.118	1.118	1.118
Initial position Z_0 (bohrs)	17.0	17.0	17.0
Average initial momentum k_{Z_0} (atomic units)	7.349	7.349	7.349
Basis set parameters			
N_x, N_y	10		
M_{dif}		5	5
N_{dif} (N_{xy} for CCWP)	100	61	12
N_z	80	80	80
Grid spacing ΔZ (bohr)	0.25	0.25	0.25
Lattice parameter a (Å)	2.84	2.84	2.84
Maximum value of j in basis j_{max}	6	6	6
Time propagation			
Size time step (atomic units)	240	240	240
Number of time steps	255	255	255
Order of SIL method N_{lan}	9	9	9
Optical potential			
Initial value of range Z_I^{min} (bohrs)	15.75	15.75	15.75
Proportionality constant A_2 (hartrees)	0.01	0.01	0.01
Range L (bohrs)	4.0	4.0	4.0
Other			
Analysis value of Z, Z_∞ (bohrs)	15.75	15.75	15.75
Tolerance norm elastic grid tol_{sp}	10^{-10}	10^{-10}	10^{-10}
Number of grid points elastic grid	128	128	128
Cutoff potential expansion $V_{\mathrm{max}}^{\mathrm{cut}}$ (eV)	0.5	0.6	0.6
Cutoff kinetic energy T_{cut} (eV)	0.6	0.6	0.6

tion $Q(X,Y)$ of Eq. (23f)] and, therefore, $N_{\mathrm{coup}}^{\mathrm{dif}}=5$. For the Wolken potential, $C_V=1+\lambda+2\times\beta+2\times\beta\times\lambda=1.32$ for the RDWP and SAWP methods (see Sec. II C), yielding a spectral range which is larger than that of a FBR method by a factor of 1.37. For the CCWP and SNWP methods, $C_V=1+\lambda=1.24$, and the associated spectral range is 1.27 times the spectral range of the FBWP method.[59]

F. Numerical details

Calculations using the CCWP, RDWP, and SAWP methods were performed with the input parameters as given in Table IV. Most of these parameters have already been discussed in Secs. II A–II D. The average initial momentum k_{Z_0} given in Table IV corresponds to a collision energy of 0.2 eV, and all calculations were performed for normal incidence of the wave packet. The SIL method[78] was used to propagate the wave function in time. We made no systematic attempt to optimize the value of $V_{\mathrm{max}}^{\mathrm{cut}}$ for the different methods, because the spectral range obtained from using one specific value of V_{max}^{co} would not differ much for the CCWP method on the one hand and the RDWP and SAWP methods on the other hand (see Secs. II C and II E).

In all calculations, we use the empirical H_2 rotational energies as obtained from Ref. 87, rather than treating H_2 as a rigid rotor. In the RDWP and SAWP calculations, the A_2 parameters given in Table IV represent maximum values, and we obtain channel dependent optimal A_2 values using linear interpolation of Table III of Ref. 82. In this procedure, E and λ as defined in Table III of Ref. 82 are calculated using $E=E_{\mathrm{col}}$-channel energy, where E is the translational energy of the scattered channel that is associated with the translational motion normal to the surface.

In the CCWP method, when performing the FFT's for a given rotational state the wave function is held in an array $ar(nz,ny,nx)$, where the first dimension is for Z, etc. The FFT's were performed consecutively using the scilib Cray routine MCFFT, vectorizing along Y and X when performing the FFT's in Z, vectorizing along Z when performing FFT's along Y, and vectorizing along Z and Y when performing FFT's along X. Care was taken to avoid memory bank conflicts. The three-dimensional (3D) FFT routine CFFT3D is very inefficient for low values of N_x and N_y,[88] but the efficiency of the algorithm outlined above and using MCFFT is comparable[89] to that of a sophisticated algorithm using rotations to obtain optimized vector lengths.[88] For $N_z=80$ and $N_x, N_y=10$ the algorithm using MCFFT is faster than CFFT3D by a factor 4. For these values of N_z and N_x and N_y (80,10,10), on a Cray C-90 about 37% of the cpu time required for a full 3D FFT is spent on the transforms along Z, the transforms along X and Y taking the remainder of the cpu time.

III. RESULTS AND DISCUSSION

Results of scattering calculations employing the CCWP, RDWP, and SAWP methods are given in Table V. As should be the case, identical results were obtained using the RDWP method and its symmetry adapted version (SAWP). The results of the CCWP method, on the one hand, and the other two methods, on the other hand, differ slightly because, effectively, a different diffractive basis set is used in the CCWP calculations (see Sec. II B). The number of diffrac-

TABLE V. Probabilities for rotationally and diffractionally inelastic scattering of H_2 (initial rotational state $j=0$) from LiF(001) are given for the CCWP, RDWP, and SAWP methods. The collision energy is 0.2 eV. The results are for normal incidence.

j'	n	m	CCWP	RDWP, SAWP
0	0	0	0.8367(−1)[a]	0.8362(−1)
	1	0	0.6284(−1)	0.6282(−1)
	2	0	0.7382(−2)	0.7382(−2)
	1	1	0.4521(−1)	0.4520(−1)
	3	0	0.2774(−3)	0.2778(−3)
	2	1	0.5028(−2)	0.5026(−2)
2	0	0	0.6167(−1)	0.6169(−1)
	1	0	0.4427(−1)	0.4426(−1)
	2	0	0.4849(−2)	0.4850(−2)
	1	1	0.3030(−1)	0.3031(−1)
	3	0	0.1585(−3)	0.1585(−3)
	2	1	0.3128(−2)	0.3128(−2)

[a] The notation (−1) means $\times 10^{-1}$

tive states effectively present in the CCWP calculation is 100, whereas only 61 states are present in the RDWP calculation employing a diamond shaped grid, the diffraction basis containing states of diffraction order up to 5. Nevertheless, we find that using a maximum diffraction order of 5 in the basis set is good enough for obtaining converged results for diffractive scattering where the diffraction order is 0–3, as was found previously in CC calculations employing the same collision energy, but a different angle of incidence. Thus, an advantage of the method employing a full close-coupling representation is that fewer diffractive states can be used in the basis set.

The cpu times as obtained for calculations on a Cray C-90 are given in Table VI for the CCWP, RDWP, and SAWP methods. The numbers given for the SNWP method are estimates based on the scaling relations discussed in Sec. II B. As can be seen from Table VI, in the CCWP calculation the cpu time spent on performing the potential energy operation is much less than the cpu time spent in performing the FFT's along X and Y. In such a case, the full close-coupling RDWP method may be expected to be faster, which indeed is the case for the present example: The RDWP method is faster by a factor 1.8. The gain is much more spectacular when use is also made of symmetry, the SAWP method being faster by a factor 8.6.

TABLE VI. CPU times (on a Cray-C90, in seconds) are given for calculations on rotationally and diffractionally inelastic scattering using the CCWP, the RDWP, and the SAWP methods. The numbers given for the SNWP method are estimates.

Operation	CCWP	RDWP	SAWP	SNWP
SIL algorithm	5.43	3.02	0.68	1.14
V_I	0.90	0.49	0.11	0.19
K, multiplications	0.96	0.56	0.12	0.20
K_z, FFT's	7.88	4.52	1.15	1.65
K_{dif}, FFT's	13.43			3.36
Potential	2.99	8.41	1.40	0.63
Overhead	1.01	0.97	0.32	0.30
Total	32.60	17.97	3.78	7.47

In general, the scaling relations of Table I are well obeyed. For instance, in the RDWP method the cost of performing the FFT's along Z should be 61% of the cost in the CCWP method, the actual number is 57%. The deviation is probably due to the difference in vector length, the length in the RDWP method (61) being nearly optimal (64 on a Cray C-90). In the SAWP method, the cost of performing the FFT's is 14% that of the cost in the CCWP method, compared to a value of 12% predicted by the scaling relations. In the SAWP calculation, the vector length is 48, the FFT's being performed for all rotation-diffraction states together.

In performing the potential energy operation, the scaling of the RDWP and SAWP methods is somewhat more favorable than that predicted in Table I, the expressions in Table I being upperbounds. The number $N_{\mathrm{coup}}^{\mathrm{dif}}$ represents the maximum number of diffraction states a diffraction state may couple to. The actual number of states coupled to may be less for a given state, if it lies on a ''border'' of the momentum grid. If we consider for a moment a diffraction only calculation (one rotational state), the scaling relation predicts that $5\times61=305$ multiplications should be carried out per grid point in Z, the actual number (of nonzero matrix elements in the diffractional potential coupling matrix) is 261. Therefore, while the scaling relation predicts the potential energy operation to be 3.05 (5×0.61) times more expensive in the RDWP method than in the CCWP method, the actual number is 2.81.

For all operations, except the transformations along X and Y and the overhead, reliable estimates of the cost of these operations in the SNWP method can be calculated by multiplying the CCWP values by a factor 0.21 (see Sec. II B). The overhead of the SNWP method was taken as that of the SAWP method. The cost of performing the symmetry adapted DVR transformation to calculate the diffractive kinetic energy was estimated as follows. For $N_x=8$, a comparison of the cost of transforming along X using the FFT method (0.16) and using the DVR method (0.43) is given by Lemoine in Table I for the case that symmetry is not used. To get the cost of also transforming along Y using no symmetry, multiply the cost of the FFT method by a factor of 2. To get the cost of the DVR method using symmetry, divide by 5. We then find that using the symmetry adapted DVR method should be less expensive by a factor of 4 than performing FFT's along X and Y as is done in the CCWP method. Thus, the cost of transforming along X and Y is calculated by dividing the cost of the CCWP method for this operation by 4. The resulting total cpu time required by the SNWP method is approximately twice that of the SAWP method. Thus, for normal incidence, and for the admittedly favorable case of the H_2+LiF(001) Wolken problem, it is more advantageous to use symmetry adapted functions within a full VBR than using only symmetry needed functions in a mixed approach (FBR for the diffractive degrees of freedom and VBR for the rotations).

An estimate of how efficient the methods are for problems for which a basis set of different size is needed can be obtained from the scaling relations. All CPU times for problems in which a different value of N_{rot} needs to be used can be obtained by multiplying with one and the same factor. For problems in which more diffraction states need to be used in

TABLE VII. Estimated CPU times (on a Cray-C90, in seconds) are given for calculations on rotationally and diffractionally inelastic scattering for $N_{\text{coup}}^{\text{rot}}=5$ and $N_{\text{coup}}^{\text{diff}}=5$ using the CCWP, the RDWP, the SAWP, and SNWP methods. All results are scaled so that the total cpu time in the CCWP method is 100 for $N_{\text{coup}}^{\text{rot}}=3$ and $N_{\text{coup}}^{\text{dif}}=5$.

Operation	CCWP	RDWP	SAWP	SNWP
SIL algorithm	16.65	9.26	2.09	3.50
V_I	2.76	1.50	0.34	0.58
K, multiplications	2.94	1.72	0.37	0.61
K_z, FFT's	24.17	13.86	3.53	5.06
K_{dif}, FFT's	41.19			10.31
Potential	15.28	43.07	7.16	3.22
Overhead	3.10	2.97	0.98	0.92
Total	106.1	72.38	14.47	24.2

the basis set, the fully close-coupled methods become slightly more favorable, because the transformations along X and Y are avoided in these methods.

An idea of how efficient the methods are relative to one another in case a different, more anisotropic or more corrugated, potential is used (where the potential is still independent of ϕ, however) can also be obtained from the scaling relations. Here we only consider the case where the same numbers can be used for N_{xy}, N_{dif}, and N_{rot}.

To work out the relative efficiency of the methods for a more anisotropic or more corrugated potential, all we have to do is calculate how the cost of performing the potential energy operation changes. To do so, we first scaled all the numbers of Table VI by multiplying all numbers with 3.067, so that the total cost of the CCWP method comes out as 100. Next, we apply the scaling relations to the calculation of the cost of the potential energy operation. Results are given in Table VII for $N_{\text{coup}}^{\text{rot}}=5$ (spherical harmonics present in the potential expansion up to order 4) and in Table VIII for $N_{\text{coup}}^{\text{dif}}=13$ (fourier terms present up to order 2). As can be seen from Table VII, the methods using the full close-coupling representation are still much more efficient for increased anisotropy of the potential. As can be seen from Table VIII, the full VBR methods are also slightly more efficient for a more corrugated potential.

TABLE VIII. Estimated CPU times (on a Cray-C90, in seconds) are given for calculations on rotationally and diffractionally inelastic scattering for $N_{\text{coup}}^{\text{rot}}=3$ and $N_{\text{coup}}^{\text{dif}}=13$ using the CCWP, the RDWP, the SAWP, and SNWP methods. All results are scaled so that the total cpu time in the CCWP method is 100.

Operation	CCWP	RDWP	SAWP	SNWP
SIL algorithm	16.65	9.26	2.09	3.50
V_I	2.76	1.50	0.34	0.58
K, multiplications	2.94	1.72	0.37	0.61
K_z, FFT's	24.17	13.86	3.53	5.06
K_{dif}, FFT's	41.19			10.31
Potential	9.17	67.0	11.15	1.93
Overhead	3.10	2.97	0.98	0.92
Total	100.0	96.4	18.5	22.9

TABLE IX. Central memory requirements (in words) are given for calculations on rotationally and diffractionally inelastic scattering using the CCWP, RDWP, SAWP, and SNWP methods.

Memory for	CCWP	RDWP	SAWP	SNWP
V	80 000	208 800	33 600	16 800
Wave function (L)	640 000	390 400	76 800	134 400
Wave function (C)	256 000	156 160	30 720	53 760
Total (L)	720 000	599 200	110 400	151 200
Total (C)	336 000	364 800	64 320	70 560

If the potential is both more corrugated and more anisotropic, the methods employing a VBR only for the rotational degree of freedom will be more efficient, also because these methods need less memory to store the potential coupling matrix. However, even in realistic molecule-surface potentials, Fourier terms of order 2 and higher are likely to be significant only at short range. Similarly, one would also expect terms associated with spherical harmonics of order higher than 2 to become significant only close to the surface. This suggests that a fully close-coupled method could still be more efficient if, in the construction of the potential coupling matrix, one would take into account that the higher order terms in the potential expansion are important at short range only. Alternatively, one could also consider mixed approaches. One could use a VBR only in the rotations close to the surface, and a full VBR further away. In many cases, it may be even better to use a method employing the full finite basis representation close to the surface, as it is much easier to impose a cutoff on the potential energy in this method.[59] Imposing this cutoff should only be necessary at short range, and problems with imposing this maximum in a VBR method will be removed completely if an FBR is used at short range.

The memory requirements of the different methods for the present computational problem are given in Table IX, both for the Chebychev propagation method (four storage arrays) and the SIL method of order 9 (ten storage arrays). For the Lanczos scheme, the fully close-coupled methods are more favorable. The rotationally close-coupled and fully close-coupled methods are of comparable efficiency in case the Chebychev propagation scheme is used. In a calculation requiring large amounts of memory (like a full 6D calculation on dissociative chemisorption of H_2 on a metal surface), one would typically want to use the Chebychev method, because it is cheaper in memory usage.

All results presented in this section are for a potential containing no azimuthal dependence. Applying symmetry using a symmetry adapted full close-coupling representation is not easy in case the azimuthal dependence is also present, since the dependence on ϕ has also to be considered. However, the techniques used should be fully applicable to codes employing the time-independent CC method, where larger gains should be expected from using symmetry, as the computational cost scales with the cube of the number of states present in the basis set. Moreover, we have demonstrated that a considerable gain in efficiency can be obtained using symmetry adapted functions for a model problem containing little anisotropy and corrugation in the potential. It is likely that gains in efficiency can be made for realistic problems as well, either by constructing the potential coupling matrix in such as way as to take into account that higher order terms in the potential expansion will be significant only at short range, or by applying the fully close-coupled method only at medium and long range (not close to the surface), in a mixed approach. It now remains to test the usefulness of the method for more realistic molecule-surface problems where the potential also contains a ϕ dependence. We hope to report on such studies in the near future.

IV. CONCLUSIONS

We have tested the performance of a fully rotationally and diffractionally close-coupled wave packet method, and the performance of its symmetry adapted version (the SAWP method). The cost of the potential energy operation scales semilinearly with the number of rotation-diffraction states present in the basis set, provided that the sparseness of the potential coupling matrix is taken into account in performing the matrix-vector multiplications required to evaluate the action of the Hamiltonian on the wave function.

The method was tested on an admittedly favorable system, i.e., the H_2+LiF(001) Wolken model system. The model potential used contains no azimuthal dependence, and little anisotropy and corrugation. For this model system and using no symmetry, we find the fully close-coupled method to be twice as efficient as the method employing a close-coupling representation only in the rotational degree of freedom, the close-coupling wave packet (CCWP) method. Likewise, it is more advantageous to use symmetry adapted functions within the full close-coupling presentation than using only symmetry needed functions in a mixed approach (FBR for the diffractive degrees of freedom and VBR for the rotations), the SAWP method being twice as fast as the symmetry adapted version of the CCWP method. For normal incidence, the SAWP method is faster than the conventional (not symmetry adapted) CCWP method by almost an order of magnitude.

In this work, we do not investigate the efficiency of the SAWP method for molecule-surface potentials also containing a dependence on the azimuthal angle of orientation. In realistic molecule-surface problems, the anisotropy and corrugation may be large close to the surface, and the full close-coupling representation may be less favorable at short range. In such a case, the fully close-coupled method may still be more efficient, provided that the construction of the potential coupling matrix is done in a way which takes into account that higher order terms are likely to be significant only at short range. Moreover, it may be useful to combine different representations for different ranges of the scattering grid in wave packet calculations. It is our plan to address these matters in the near future, by performing additional research on more realistic molecule-surface problems.

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