Variational wave packet method for dissipative photodesorption problems

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Abstract

A recently introduced variational wave packet method to integrate the time-dependent Liouville–von Neumann equation for open quantum systems is adapted here for one- and two-dimensional models describing the photodesorption of a neutral molecule from a dissipative metal surface. By comparison to benchmark results, we find that any quantities of interest can be converged with any desired accuracy within the variational wave packet scheme. The method is general, shows uniform convergence properties and is computational efficient.

1. Introduction

For the understanding of the dynamics, the spectroscopy, or the chemical behaviour of molecules in bulk solids, in matrices, in solution, or at solid surfaces, the consideration of the (possibly thermal) condensed phase environment is of vital importance. One popular and powerful way to couple the nuclear dynamics of a molecule, say, to a “bath”, is open-system density matrix theory. Within this approach, a Liouville–von Neumann (LvN) equation for the density operator \( \hat{\rho} \) of the form (atomic units, \( \hbar = 1 \))

\[
\dot{\hat{\rho}}(t) = -i\left[ \hat{H}, \hat{\rho} \right] + \mathcal{L}_D \hat{\rho}
\]  

(1.1)

has to be solved subject to some initial condition, \( \hat{\rho}(t = 0) \). Here, \( \hat{H} \) is the system Hamiltonian depending (on the typically few) strongly coupled system modes only. \( \mathcal{L}_D \hat{\rho} \) gives the evolution in time of the system density operator due to the coupling of the system to an unobserved environment (\( \mathcal{L}_D \) is the dissipative Liouvillian superoperator) and thus accounts for energy and phase relaxation. Under the Markov approximation (i.e. when memory effects are neglected), \( \mathcal{L}_D \hat{\rho}(t) \) is a function only of \( \hat{\rho}(t) \). The Redfield theory [1] on the one hand and the dynamical semigroup approach by Lindblad on the other [2], constitute the most prominent Markovian approaches to open quantum systems.

Except for special examples, the open-system LvN equation (Eq. (1.1)) must be solved numerically. There are two main approaches to do so. Using a direct strategy, (1.1) is solved by a single matrix propagation. In indirect schemes, (many) different wave packet propagations must be carried out instead. The direct approaches are usually general (i.e. they are equally applicable to Redfield and Lindblad forms of dissipation) and they solve a given LvN equation, in principle “exact”. Various efficient, direct approaches have been suggested in recent years. These methods differ in their choice of the
basis to represent the operators [3–7] and/or with respect to the approximation of the time-evolution (super-) operator [3,4,6,8,9]. A drawback of the direct methods is their unfavourable memory requirements, which scale typically as \( N^2 \), where \( N \) is the dimension of the relevant system Hilbert space.

Here, the wave-packet based, indirect methods offer considerable savings, because only \( N \)-component wavefunctions have to be propagated. However, this has to be done \( n \) times. Nevertheless, when \( n < N \), even a speedup in computation time is possible, relative to the direct methods. Examples for efficient wave packet approaches to open quantum systems are the Monte Carlo wave packet method (MCWP) [6,10,11] and the quantum state diffusion method [6]. The wave packet methods are not always general (i.e. they may be restricted to dissipation of Lindblad form [10]) and – as stochastic approaches – they sometimes converge only poorly to the exact results, in particular when these are dominated by statistical rare events [12].

Recently, a variational wave packet (VWP) method was suggested [13], which solves an open system LvN equation with a minimum number of wave packets. This method was applied, in a zero-order state basis, to a bound, dissipative problem [11], for which three system modes and three system electronic states had to be considered.

The aim of the present Letter is to adapt the VWP method for the problem of photoinduced desorption of a molecule (NO) from a metal surface [Pt(111)]. This so-called DIET-process (desorption induced by electronic transitions) proceeds via ultrashort-lived excited intermediates and has previously been formulated within the language of open-system density matrix theory and treated with direct [12,14,15] as well as stochastic wave packet methods [12,15]. The challenge of the problem is twofold. First, since bonds are to be broken, a coordinate (grid) representation is chosen, leading to large Hilbert space dimensions \( N \), in particular for multi-mode models [15]. Secondly, the desorption probabilities are typically small (10\(^{-4}\), say) and therefore stochastic wave packet methods converge slowly when properties of the desorbates are of interest, as shown in Ref. [12]. We will address the question as to whether the VWP method can outperform the direct or stochastic density matrix propagation schemes.

2. The variational wave packet method

In the VWP method [13], the following ansatz is made for the open-system (reduced) density matrix

\[
\hat{\rho} = \sum_{u=1}^{N} \sum_{v=1}^{N} \rho_{uv}(t) |\psi_u(t)\rangle \langle \psi_v(t)|.
\]

(2.1)

where \( |\psi_u(t)\rangle \) are time-dependent expansion wavefunctions and \( \rho_{uv}(t) \) their time-dependent coefficients. By (i) using a Dirac–Frenkel type variational principle, (ii) choosing the wavefunctions to be orthonormal at all times and (iii) working in a diagonal representation for \( \hat{\rho} \) (with \( \rho_{uu} = \rho_u \)), it has been shown that Eq. (2.1), when inserted in the variational principle equivalent to Eq. (1.1) leads (apart from an unimportant arbitrary phase factor in the wavefunctions) to the following, coupled set of equations of motion [13] for the expansion coefficients

\[
\frac{\partial \rho_u(t)}{\partial t} = \langle \psi_u(t)| \mathcal{L}_D \hat{\rho} |\psi_u(t)\rangle
\]

(2.2)

and wavefunctions

\[
\frac{\partial |\psi_u(t)\rangle}{\partial t} = -i\hat{H}_1 |\psi_u(t)\rangle + i\hat{H}_2 |\psi_u(t)\rangle
\]

\[
\times \langle \psi_u(t)| \hat{H}_1 |\psi_u(t)\rangle + \langle \psi_u(t)| \hat{H}_2 |\psi_u(t)\rangle
\]

\[
+ \sum_{v=1,v \neq u}^{N} \frac{1}{\rho_u(t) - \rho_v(t)} |\psi_v(t)\rangle \langle \psi_v(t)|
\]

\[
\times \langle \psi_v(t)| \mathcal{L}_D \hat{\rho} |\psi_u(t)\rangle + \frac{1}{\rho_u(t)}
\]

\[
\times (1 - \hat{P}) \mathcal{L}_D \hat{\rho} |\psi_u(t)\rangle.
\]

(2.3)

where \( \hat{P} = \sum_{v=1}^{N} |\psi_v(t)\rangle \langle \psi_v(t)| \). In Eq. (2.3), the first term on the r.h.s. is due to the Hamiltonian evolution of the system and the second one determines the phase factor of the wavefunction \( |\psi_u(t)\rangle \). The third and fourth terms account for the coupling of the system to the dissipative environment. When a complete set of expansion wavefunctions is used, the fourth term vanishes due to the projector \((1 - \hat{P})\) and the trace of the density matrix is conserved. For finite \( n \), however, the trace decreases with increasing time and this loss of norm can be used as a convergence criterion for the proper choice of the number of expansion coefficients, \( n \). In practice, one starts initially with a small number of basis functions and adds new functions during the propagation as soon
as the total norm drops below some prespecified threshold [13]. Further, a regularization scheme is adopted to cope with possible singularities associated with the term \((1/(\rho_s(t) - \rho_i(t)))\) in Eq. (2.3).

3. Open-system density matrix model for desorption of NO from Pt(111)

For the DIET of NO from Pt(111), the same one- and two-mode, two-state models are used as previously [14,15]. Since in DIET (in contrast to DIMET, "desorption induced by multiple electronic transitions") multiple excitations of the adsorbate are not possible [14], only a single dissipative channel (namely the electronic decay) is allowed for. Assuming a Lindblad form for the dissipation, the relevant Lindblad–LvN equation reads

\[
\dot{\rho}(t) = -i[H_i, \rho] + \left(\hat{C} \rho \hat{C}^\dagger - \frac{1}{2} \left[\hat{C}^\dagger \hat{C}, \rho\right]\right),
\]

(3.1)

where \(\hat{C}\) is a "Lindblad operator", specifying the environment-induced electronic relaxation (see below).

The system Hamiltonian \(H_i\) in Eq. (3.1) is of the simple, uncoupled two-state form

\[
\hat{H}_i = \hat{H}_g |g\rangle \langle g| + \hat{H}_e |e\rangle \langle e|,
\]

(3.2)

where \(|g\rangle\) and \(|e\rangle\) stand for the electronic ground and the (short-lived) electronic excited states, respectively. The Hamiltonians \(\hat{H}_i (i=g,e)\) are in the one-[14] and two-mode [15] models given by

\[
\hat{H}_i = -\frac{1}{2} \sum_{j=1}^{F} \frac{\beta_j^2}{\mu_j} \delta_{j} + V_i(|Q_i|).
\]

(3.3)

Here, in the one-dimensional case \(F=1, Q_1 = Z\) (the distance of the molecular center-of-mass to the surface) and \(\mu_1 = m_{NO}\), while in the two-mode case \(F=2, Q_1 = Z_1 Q_2 = m_{NO}\) \((r\) is the NO bond length) and \(\mu_2 = (m_{NO} + m_{NO})/m_{NO} + m_{NO}\).

Eq. (3.1) is solved subject to the initial condition \(\dot{\rho}(0) = |e\rangle \langle e| \otimes |0_g\rangle \langle 0_g|\), i.e. an initial, singular Franck–Condon transition of the vibrational and electronic ground state wavefunction \(|0_g\rangle\) to the electronic excited state \(|e\rangle\) is assumed, as a crude model for an indirect, "hot-electron" mediated excitation step [14].

Once electronically excited, the wave packet starts to move and is at the same time electronically quenched. The quenching is controlled by the Lindblad operator \(\hat{C}\),

\[
\hat{C} = \sqrt{\Gamma_{eg}} |g\rangle \langle e|,
\]

(3.4)

where, \(\Gamma_{eg} = 1/\tau\) is the rate for the decay of the excited state \(|e\rangle\) to the ground state \(|g\rangle\) (and \(\tau\) is the excited state lifetime). For simplicity, \(\Gamma_{eg}\) is assumed to be coordinate-independent. Generalization to coordinate-dependent, non-exponential decay is straightforward and possible without much additional effort for all numerical approaches adopted below.

After a final propagation time \(t_{\text{max}}\), those parts of the wave packets which have reached asymptotic regions \(Z > Z_{\text{des}}\) of the ground state potential energy surface are counted as "desorbed" and are analyzed. Of particular interest are the desorption probability \(P_{\text{des}}\) and the "translational temperature" \(T_{\text{trans}} = E_{\text{trans}}/2 k_B\) of the desorbrates \(E_{\text{trans}}\) is the kinetic energy of the neutral, desorbing NO molecules and \(k_B\) is Boltzmann’s constant). Since the desorption probability is small in the cases considered below, the properties associated with adsorbates are called "in-frequent properties" in the following. Occasionally, we will also be interested in "frequent properties", namely the populations of the excited and ground states, and the total system energy.

The VWP results, which are obtained with \(n\) basis wavefunctions (excited and ground state basis) are always checked against "exact" benchmark calculations. In the one-mode model, the exact reference is provided by direct density matrix propagation, based on a Newton polynomial expansion of the time-evolution superoperator (see Refs. [4] and [14] for details). For the two-mode model a direct density matrix result is at present not available. Here, the results of a "jumping wave packet & incoherent, weighted averaging scheme" [16], which can be shown to be equivalent to density matrix theory for DIET models (single dissipative channel) with coordinate-independent quenching rates [12] are used (in this case, the weighting functions are known analytically. For an extension of the economic "jumping & weighted average" approach to coordinate-dependent quenching, see Ref. [15]). In the "jumping wave packet" calculations, a split-propagator is used, while for the VWP calculations a predictor-corrector integrator with adjustable time-steps is adopted [13].
For any method to solve (3.1), a discrete coordinate-space representation is chosen for all occurring operators and wavefunctions. The action of the kinetic energy operator is evaluated locally, by using a discrete fast fourier transform (FFT) algorithm [4].

4. One-dimensional model

In the one-dimensional model, the ground state potential \( V_r(Z) \) is a Morse function and the excited state \( V_r(Z) \) is an image-charge stabilized bound, negative-ion resonance state [16]. The potential parameters are given in Ref. [14] and the potential curves are shown in Fig. 1 of that reference. The discrete grid used consists of \( N = 512 \) points and the excited state lifetime is taken as \( \tau = 2 \) fs. All other computational parameters and procedures are described in Ref. [14].

Let us first consider “frequent” properties associated with the decay of the excited state resonance, namely \( N(t) \) (the population of the excited state), \( N_{to}(t) = N_1(t) + N(r) \) (the total norm) and \( E_{tot}(t) \) (the total system energy). As shown elsewhere [12], these properties can be accurately computed with a moderate number of wave packets within the “jump & averaging” scheme and even with the ordinary MCWP method.

Table 1 demonstrates that the VWP method, being variational, is even more economic in the sense that a smaller number of wavefunctions \( n \) is required for a certain accuracy. In the table, for the selected times \( t = 2, t = 5, t = 20 \) and \( t = 50 \) fs the relative error for each observable \( A(t) \) (\( A = N, N_{to} \) and \( E_{tot} \)),

\[
E[A(t); n] = \frac{A_{ex}(t) - A_{VWP}(t; n)}{A_{ex}(t)}
\]

(4.1)

is given for different basis set sizes \( n \) of the VWP expansion (2.1). In these calculations, \( n \) was kept fixed over the entire propagation time. \( A_{ex}(t) \) in Eq. (4.1) denotes the “exact” observable, while \( A_{VWP}(t; n) \) is the result of a VWP calculation with \( n \) functions. Actually, the exact, frequent observables are known analytically or semi-analytically in the present example \([N_1(t) = e^{-r(t)}, N(t) = N_1(t) \cdot E_{tot}(0) + (1 - N_1(t)) \cdot E_{tot}(\infty)]\), or can be taken from the direct density matrix propagation. However, we prefer to define as the exact results those obtained with the VWP method and \( n = 13 \), \( A_{ex}(t) = A_{VWP}(t; n = 13) \), to not spoil our analysis with (small) errors due to numerics.

Indeed, the VWP results for the frequent properties are well-converged with respect to \( n \) for \( n = 13 \); the \( n = 13 \) results itself agree to within about \( 10^{-4} \) with the (semi-) analytical ones. From this fact alone we anticipate that the VWP method may offer great computational savings over direct density matrix propagation schemes.

Table 1 shows that the “frequent” properties can be computed, to reasonable accuracy, already with much less effort. For instance, the excited state population \( N_1(t) \) is exactly reproduced with a single wavefunction, i.e., with \( n = 1 \). This observation follows also from an analytic solution of the VWP equation (Eq. (2.2)) for the expansion coefficients. Namely, if only a single excited state wavefunction \( |\psi_1\rangle \) spans the basis, the density operator \( \hat{\rho} \) in Eq. (2.1) is given by \( \hat{\rho} = r_1|\psi_1\rangle \langle \psi_1| \); further, by using

| Table 1 Computation of “frequent” properties for the DIET of NO from Pt (see text). Shown are the relative errors as defined in Eq. (4.1), for different numbers of basis functions \( n \) used in the VWP expansion |
|---|---|---|---|---|
| \( t \) / fs | 2 | 5 | 20 | 50 |
| \( N_e \) \( n = 1 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) |
| \( N_e \) \( n = 2 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) |
| \( N_e \) \( n = 3 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) |
| \( N_e \) \( n = 6 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) |
| \( N_e \) \( n = 9 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) | \(< 1.1(8)\) |
| \( N_{to} \) \( n = 1 \) | 6.32(1) | 9.18(1) | 1.00(0) | 1.00(0) |
| \( N_{to} \) \( n = 2 \) | 9.76(3) | 6.30(2) | 1.12(1) | 1.20(1) |
| \( N_{to} \) \( n = 3 \) | 7.60(5) | 2.94(3) | 2.29(2) | 2.29(2) |
| \( N_{to} \) \( n = 6 \) | \(< 1.1(8)\) | 3.00(8) | 5.03(4) | 5.46(4) |
| \( N_{to} \) \( n = 9 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | 1.10(5) | 2.30(5) |
| \( E_{tot} \) \( n = 1 \) | 3.23(2) | 2.16(1) | 1.00(0) | 1.00(0) |
| \( E_{tot} \) \( n = 2 \) | 1.42(3) | 3.98(2) | 3.74(1) | 3.75(1) |
| \( E_{tot} \) \( n = 3 \) | 3.70(7) | 2.89(3) | 1.30(1) | 1.31(1) |
| \( E_{tot} \) \( n = 6 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | 6.56(3) | 7.53(4) |
| \( E_{tot} \) \( n = 9 \) | \(< 1.1(8)\) | \(< 1.1(8)\) | 1.85(4) | 4.51(4) |

The “exact” reference is taken to be the result of the VWP \( n = 13 \) calculation. The numbers in parentheses (m) denote exponents (\( 10^m \)).
the single DIET–Lindblad operator $\hat{\mathcal{L}}$ as defined in Eq. (3.4), we have $\mathcal{L}_\rho \rho = \Gamma_g | \langle g | e \rangle \langle e | g \rangle - 1 e \rangle \langle e | \rho - 1 \rho e \rangle \langle e | \rho \rangle$. As a consequence, the equation of motion for the coefficient $\rho_1(t)$ (Eq. (2.2)) reads

$$\frac{\partial \rho_1(t)}{\partial t} = -\Gamma_{ee} \rho_1.$$  

(4.2)

With $\rho_1(t) = N_e(t)$ and $\rho_1(0) = N_e(0) = 1$ it follows, that

$$N_e(t) = e^{-\Gamma_{ee} t},$$  

(4.3)

which is the analytical result. Any errors, relative to the analytical result of $N_e(t)$ (and any other excited state property) obtained with the VWP method and $n = 1$ are therefore numerical and not due to a too small basis set. Since in the simple DIET model used here no reexcitations are possible and no Hamiltonian couplings between $|g\rangle$ and $|e\rangle$ exist, a single wavefunction is sufficient for describing the excited state dynamics throughout.

Of course, for $n = 1$ the basis is (except at $t = 0$) incomplete and total norm is not conserved; the loss of norm increases with time according to $\Delta N_{\text{tot}}(t) = 1 - e^{-\Gamma_{ee} t}$. Hence, to compute the total norm (or any observable associated not solely with the excited state), ground state basis functions $|\psi_{gs}\rangle$ must to be added. Table 1 shows, that one additional wavefunction in addition to the single wavefunction describing the excited state ($n = 2$) already suppresses (for $t = 2$ fs) the relative error from 0.632, to below $10^{-2}$. This corresponds to an increase of the total norm from 0.3677 ($n = 1$), to 0.9902 ($n = 2$). When propagated to longer times, more and more wavefunctions are needed for a certain accuracy. To reach a total norm larger than 0.9999, say, requires $n = 3$ at $t = 2$ fs, $n = 4$ at $t = 5$ fs and $n = 6$ at $t \geq 20$ fs (when the dissipation becomes inefficient). For all $t$, relative errors of the total norm (and also of the total system energy $E_{\text{tot}}$, for example) of $10^{-3}$ (and mostly much lower) are typical with $n = 6$. This is better than what was possible with the MCWP method (where in the order of $n \approx 100$ wave packet runs were needed for a comparable accuracy of the “frequent” properties [12]), and also with the “jump & average” method (which required around 30 wave packets [12]).

A more stringent test of the VWP method is its performance for “infrequent” properties, i.e. those associated with the desorption of neutral NO molecules. In Fig. 1, the desorption probability $P_{\text{des}}(t)$ is given for different basis set sizes $n$. The number of basis functions (and the time step used by the propagator) is now automatically adjusted during the propagation and $n$ is to be understood as the number of functions used at $t = t_{\text{max}} = 500$ fs. The four curves shown in the figure are for $n = 7, 9, 11$ and 13, respectively. Also shown (as bullets) are the benchmark direct density matrix probabilities taken from Ref. [14], which on the scale of the figure cannot be distinguished from the most accurate VWP calculation ($n = 13$). Both “exact” curves rise after $t \approx 100$ fs from essentially zero, to the final $t = t_{\text{max}} = 500$ fs desorption probability of $\approx 9.5 \times 10^{-5}$. This small probability is not easy to capture by stochastic wave packet methods, for which even $n = 1500$ wave packets were found to not accurately reproduce the final $P_{\text{des}}$ [12].

By contrast, the VWP method not only converges with $n = 13$, but also with a fewer number of wave packets “reasonable” results are obtained; further, the convergence to the exact result is uniform and monotonic, rather than erratic as in the MCWP method. However, to compute “infrequent” properties, certainly more basis functions are necessary than for the “frequent” ones.

This is quantitatively analyzed in Table 2, where the final ($t = t_{\text{max}}$) desorption probability $P_{\text{des}}$, the translational temperature of the desorbates $T_{\text{trans}}$, and a few other useful quantities are given, for the four VWP calculations shown in Fig. 1 and for the direct density matrix benchmark calculation. Taking the

![Fig. 1. Time-resolved desorption probabilities $P_{\text{des}}(t)$ for NO from Pt(111) (one-mode model), as obtained with the VWP method with different basis set sizes (curves) and with the direct density matrix method [14] (bullets).](image-url)
Table 2
Computation of “infrequent” properties for the DIET of NO from Pt (see text)

<table>
<thead>
<tr>
<th>Number of wavefunctions $n$</th>
<th>$P_{\text{rel.}}$ in $P_{\text{best}}$</th>
<th>$T_{\text{trans}}$ (K)</th>
<th>$T_{\text{trans}}$ (K)</th>
<th>Loss of total norm</th>
<th>Relative comp. time</th>
<th>Relative memory req.</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>3.28 ($-5$)</td>
<td>6.54 ($-1$)</td>
<td>491.3</td>
<td>4.68 ($-1$)</td>
<td>2.7 ($-4$)</td>
<td>0.06</td>
</tr>
<tr>
<td>9</td>
<td>8.42 ($-5$)</td>
<td>1.11 ($-1$)</td>
<td>786.8</td>
<td>1.48 ($-1$)</td>
<td>3.4 ($-5$)</td>
<td>0.15</td>
</tr>
<tr>
<td>11</td>
<td>9.39 ($-5$)</td>
<td>8.45 ($-3$)</td>
<td>907.2</td>
<td>1.75 ($-2$)</td>
<td>4.0 ($-6$)</td>
<td>0.45</td>
</tr>
<tr>
<td>13</td>
<td>9.48 ($-5$)</td>
<td>$-1.06$ ($-3$)</td>
<td>923.5</td>
<td>$-1.08$ ($-4$)</td>
<td>5.1 ($-7$)</td>
<td>1</td>
</tr>
<tr>
<td>direct</td>
<td>9.47 ($-5$)</td>
<td>–</td>
<td>923.4</td>
<td>–</td>
<td>–</td>
<td>$\approx 2$</td>
</tr>
</tbody>
</table>

Shown are the final ($t = t_{\text{max}}$) desorption probabilities, the translational temperatures, the relative errors (Eq. 4.1) in these quantities, the loss of total norm and the computational resources needed (the latter relative to the VWP ($n = 13$) calculation). The “exact” reference is taken to be the direct density matrix benchmark calculation of Ref. [14], which is also included in the table.

The direct density matrix result as the “exact” observable $A_{\text{ref}}$ in Eq. (4.1), we find moduli of the relative errors in the desorption yields between $1 \times 10^{-3}$ for $n = 13$ and $\approx 0.65$ for $n = 7$ (the different sign of the errors for $n = 13$, suggests that this most accurate VWP propagation is in fact slightly more accurate than the numerical direct density matrix result [14]). Similar relative errors are found for the translational temperatures.

Table 2 also shows that the relative error in the desorption yield, say, correlates almost linearly with the loss of norm. Hence, errors in the infrequent properties may be brought to a minimum by controlling the conservation of norm, which is a useful tool in cases where the exact answer is unknown.

Table 2 further tries to compare the direct density matrix propagation with the VWP method with respect to the computational effort. To make the analysis as machine-independent as possible, computation time and memory requirements are given in units of the effort for the VWP ($n = 13$) calculation.

The VWP method is clearly superior to the direct approach in terms of memory needs. The ideal, theoretical ratio between the memory requirements for the VWP method with $n$ basis vectors of length $N$ each and the direct density matrix approach (ma-

Table 3
Eigenvalues of the (ground state block of the) density matrix (right column), compared to the ground state expansion coefficients of the variational wave packet method, for different $n$, at $t = t_{\text{max}}$

<table>
<thead>
<tr>
<th>$n = 7$</th>
<th>$n = 9$</th>
<th>$n = 11$</th>
<th>$n = 13$</th>
<th>Density matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.88022571</td>
<td>0.880226017</td>
<td>0.880226026</td>
<td>0.880226018</td>
</tr>
<tr>
<td>2</td>
<td>0.096868957</td>
<td>0.096874711</td>
<td>0.096875082</td>
<td>0.096875098</td>
</tr>
<tr>
<td>3</td>
<td>0.017190538</td>
<td>0.017201899</td>
<td>0.017202689</td>
<td>0.017202743</td>
</tr>
<tr>
<td>4</td>
<td>0.004005631</td>
<td>0.004020574</td>
<td>0.004021669</td>
<td>0.004021746</td>
</tr>
<tr>
<td>5</td>
<td>0.001106745</td>
<td>0.001126925</td>
<td>0.001128210</td>
<td>0.001128300</td>
</tr>
<tr>
<td>6</td>
<td>0.000327787</td>
<td>0.000356115</td>
<td>0.000357609</td>
<td>0.000357715</td>
</tr>
<tr>
<td>7</td>
<td>0.000119952</td>
<td>0.000121829</td>
<td>0.000121948</td>
<td>0.000121958</td>
</tr>
<tr>
<td>8</td>
<td>0.000040422</td>
<td>0.000042752</td>
<td>0.000042890</td>
<td>0.000042901</td>
</tr>
<tr>
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The expansion coefficient of the (single) excited state wavefunction is zero.


5. Two-dimensional model

In the two-mode model, additional to the molecule-surface distance \( Z \), the NO vibrational coordinate is included. The 2D potential energy surfaces for the neutral ground state and the excited state negative ion resonance are taken from Ref. [17], with two modifications [15]: (i) the parameter for the NO equilibrium distance \( r_{\text{NO}} \) in the excited state is reduced from 2.377 \( a_0 \) to 2.193 \( a_0 \) and (ii) the energy difference between \( V' \) and \( V_0 \) at the Franck-Condon point is reduced to 1.5 eV. Compared to Ref. [15], an enlarged grid along \( r \) with \( N_r = 64 \) (grid spacing \( \Delta_r = 0.3 \ a_0 \)) and a grid along \( Z \) with up to \( N_z = 1024 \) (grid spacing \( \Delta_z = 0.2 \ a_0 \)) is used. The lifetime chosen is \( \tau = 10 \) fs, which produces somewhat larger (and numerically easier accessible) desorption probabilities than in the one-mode example. The total propagation time is \( t_{\text{max}} = 700 \) fs.

This time, no direct density matrix calculation is possible, because the grid consists of \( N = 65536 \) points and therefore \( 4 \times 2^{34} \) elements had to be stored for a single, two-state density matrix. A benchmark, however, can be provided by Gadzuk’s “jumping wave packet” algorithm [16] for the special DIET model at hand. The “jumping wave packet” calculation was performed on the full 1024 \( \times \) 64 grid, while in the more elaborate VWP calculations the grid size was adapted during the propagation.

Considering “infrequent” properties, with the “jumping wave packet” approach a final desorption probability of \( 2.45 \times 10^{-2} \) and a translational temperature of \( T_{\text{trans}} = 1840 \) K is obtained. With the VWP method, two calculations were performed. In a first calculation, \( n = 13 \) basis functions were used, leading to \( P_{\text{des}} = 1.83 \times 10^{-2} \) and \( T_{\text{trans}} = 1610 \) K. In a second calculation, \( n = 34 \) was chosen, giving \( P_{\text{des}} = 2.32 \times 10^{-2} \) and \( T_{\text{trans}} = 1860 \) K, which is (considering the differences in the numerical realization) in good agreement with the benchmark result.

Again, based on the loss of total norm, an internal accuracy check for the VWP method can be made. The loss of norm is \( \approx 10^{-3} \) for \( n = 13 \) and \( \approx 10^{-4} \) for \( n = 34 \) and the estimated relative errors are one order of magnitude larger. The calculations took around 2 and 10 days, respectively, on an Origin 2000 SGI workstation.

6. Conclusions

In summary, the recently proposed VWP method has been adapted for a dissociative, dissipative problem, where small probabilities are of interest. The two-dimensional example just given shows that a
reasonably accurate calculation even of ‘‘infrequent’’
properties is possible. This is achieved by using the
VWP scheme, which combines the advantages of the
direct density matrix approaches (generality, accu-

racy) with those of the indirect wave packet methods
(moderate memory requirements, potentially fast).
For ‘‘frequent’’ properties, the method shows excel-
lent numerical performance, in agreement with previ-
ous work [13].

We are presently applying the VWP method for
DIMET processes (in the two-mode model), where
reexcitations of the type $|g\rangle \rightarrow |e\rangle$ are possible, and
where much larger basis sets (both for the ground
and the excited states) are required. For these numeri-
cally demanding applications, an improved integra-
tion scheme for the VWP equations of motion is
needed. The VWP method requires the integration of
a set of nonlinear differential equations which is
presently done by a general purpose fourth order
predictor-corrector scheme. This general purpose in-
tegrator is inefficient compared to schemes specifi-
cally designed for wavefunction or density matrix
propagation. Construction of a more efficient integra-
tion scheme for the VWP equations of motion might
therefore enhance the CPU-time efficiency of the
VWP approach dramatically. Work along these lines
is in progress.

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Chemie’’ is gratefully acknowledged.

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