Quasi-ab initio dynamics: a test trajectory study of the $H + H_2$ reaction using energies and gradients based on scaling of the external correlation

A.J.C. Varandas, P.E. Abreu

Departamento de Química, Universidade de Coimbra, P-3049 Coimbra Codex, Portugal

Received 13 March 1998; in final form 2 June 1998

Abstract

We have carried out a test dynamics study of the prototype $H + H_2$ exchange reaction by running quasi-classical trajectories 'on-the-fly' using ab initio correlated energies which have been previously corrected semiempirically by the double many-body expansion plus scaling of the external correlation method to account for size-limitations of the one-electron basis set and configuration interaction expansion. The method is general and gives results in agreement with conventional trajectory calculations carried out on the accurate double many-body expansion potential energy surface for H_3. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

The quasi-classical trajectory (QCT) method has long been, and continues to be, a primary tool in chemical dynamics; it is computationally affordable for many polyatomic systems whereas a quantum dynamics treatment is often impractical. Crucial for the dynamics studies, either classical or quantal, is the availability of the relevant potential energy surface or surfaces that govern the motion of the nuclei. In general, they may be obtained by pointwise solution of the electronic Schrödinger equation using ab initio methods. Energy gradients, and in some cases also Hessians and higher-order derivatives, can also be obtained in this way [1–3]. However, the vast majority of dynamics studies carried out to date have employed potential energy surfaces obtained from semiempirical and empirical methods. Two major reasons contribute to this situation. First, one requires for the dynamics studies a quick and efficient method to calculate the potential energy surface and the energy gradient at any arbitrary geometry along the trajectory. Second, only in favourable cases do state-of-the-art ab initio methods reach sufficient accuracy to be of practical interest for reaction dynamics.

The traditional approach to dynamics involves therefore two basic steps: (i) fit of the calculated ab initio electronic energies (eventually corrected semiempirically) to a convenient analytical form, and (ii) integration of the classical equations of motion using some numerical technique. Clearly, the bottleneck in this approach is the modelling of the potential energy surface. Although our own double many-body expansion [4,5] (DMBE) method has proved general and particularly successful in the case of

small polyatomic systems, the construction of a global potential energy surface can be extremely difficult especially for systems with large dimensionality, say with four atoms or more. Focusing on this problem, Helgaker et al. [6] have suggested an alternative scheme to trajectory calculations, which avoids the explicit representation of the complete molecular potential energy surface. Instead of solving numerically the classical equations of motion using a global potential function, they have approximated the true potential energy surface by a sequence of model quadratic surfaces obtained from energies, gradients and Hessians. Thus, these local surfaces are calculated as needed in the course of the integration and only those parts of the potential energy surface actually traversed by the trajectory are considered. Each model quadratic surface may therefore be entirely defined from the ab initio data alone, while the equations of motion afford locally an exact analytical solution [7]. Clearly, the method is applicable to any molecule irrespectively of size, as shown by Helgaker et al. [6] in their studies of the unimolecular fragmentations of H_3 and protonated formaldehyde (CH_2OH^+). However, the relevant local surface parameters were computed from expensive multiconfiguration self-consistent-field wavefunctions in that work and hence drastic simplifications had to be made [6] on the dynamics calculations which obscured the practical value of the approach for large scale QCT calculations. More recently [8], we have tested the approach on the $H + H_2$ and $O + OH$ exchange reactions by simulating the ab initio energies from reliable DMBE functions for ground state H_3 and HO_2. Parenthetically, we note that the DMBE function for H_3 has chemical accuracy ($<$ 1 kcal mol^{-1}) and it has been judged [9] to provide the best overall description of the title reaction. Moreover, we have suggested in Ref. [8] a variant of the 'on-the-fly' trajectory approach (QCT/GH) that can be used to preserve the zero-point energy constraint along the trajectory, a well known deficiency of classical dynamics which has attracted considerable attention in recent years (Refs. [8,10] and references therein).

In the present work we suggest a method to integrate trajectories 'on-the-fly' where the amount of empiricism is reduced to a minimum level and hence refer to the approach as quasi-ab initio dynamics. Thus, we release the requirement of expensive ab initio calculations, which is commonly met when aiming at accurate dynamics calculations. Specifically, we use reasonably cheap ab initio second-order configuration interaction [11] (SOCI) energies and their first analytical derivatives and account for the unavoidable errors due to truncation of the configuration-interaction expansion and incompleteness of the one-electron basis sets by scaling the external correlation energy (this is also known as dynamical correlation and we will utilize the two notations interchangeably to conform with use in previous publications). For the scaling we will employ the DMBE-SEC (double many-body expansion plus scaling of the external correlation) method proposed some years ago by one of us [12]. In the case of a homonuclear triatomic such as H_3, the method affords as a minimal amount of empiricism two scaling parameters: one [$\mathscr{F}^{(2)}$ in Eq. (2)] gives the correct exothermicity for the reaction by reproducing the dissociation energy of each diatomic fragment; the other ($\mathscr{F}^{(3)}$) is chosen to mimic the best estimate of the barrier height (well depth in the case of a bound triatomic molecule) for the exchange reaction. Because gradients and Hessians cannot be obtained analytically from the SOCI method, we will use only numerical gradients for the dynamics simulations. Thus, we do not care to fix the problem of zero-point energy leakage in the QCT calculations reported in the present work.

2. DMBE-SEC method: a synopsis

In the DMBE-SEC method, the total energy of an N-atom system is written as [12,13]

$$V(\mathbf{R}^N) = \sum_{n=2}^{N} \sum_{\mathbf{R}^n \subset \mathbf{R}^N} \left[V_{\text{EHF}}^{(n)}(\mathbf{R}^n) + V_{\text{dc}}^{(n)}(\mathbf{R}^n) \right] \quad (1)$$

where the indices EHF and dc denote the extended Hartree–Fock [i.e. the energy calculated at the ab initio full-valence complete-active-space (FVCAS) level] and dynamical correlation parts of the energy, $\mathbf{R}^n \subset \mathbf{R}^N$ is any set of $n(n-1)/2$ interatomic distances referring to n atoms, $\mathbf{R}^N \equiv (R_1, \ldots, R_{N(N-1)/2})$ and the energies of the iso-

lated atoms are taken as the reference. In turn, the recovered fraction of the dynamical correlation is assumed to be approximately constant for each n-body term and hence the corrected n-body dynamical correlation energy assumes the form

$$V_{dc}^{(n)} = \frac{V_{FVCAS-CISD}^{(n)} - V_{FVCAS}^{(n)}}{\mathscr{F}^{(n)}} \qquad (2)$$

where FVCAS–CISD stands for the correlated energy calculated at the multireference CI singles and doubles level out of the FVCAS reference space. In this work it has been obtained from a SOCI calculation using the GAMESS [11] suite of programs. The DMBE-SEC method has been applied successfully in Ref. [12] to H_3 and HO_2 and is currently being used [14] to obtain a potential energy surface for the lowest triplet state of HOCN. The method allows therefore for different n-body scaling factors and hence includes as a particular case the SEC approach of Brown and Truhlar [15], which assumes all scaling factors to be equal ($\mathscr{F}^{(n)} = \mathscr{F}$). Note that the SEC method of Brown and Truhlar [15] requires the use of balanced basis sets, which can be time consuming and lead to deviations from the optimal

variational basis sets. Note further that Simons [16] has provided a formal justification for the SEC approach by using a size-extensive functional and showing that

$$\tilde{V}_{dc} = (V_{FVCAS-CISD} - V_{FVCAS})/c_0^2 \qquad (3)$$

where c_0 is the coefficient of the FVCAS wavefunction in the CI expansion. Thus, the SEC-method is equivalent to taking $\mathscr{F} = c_0^2$.

Fig. 1 compares the H_2 diatomic curves calculated at the various levels of ab initio theory, using the standard 6-311G(d,p) basis set of Krishnan et al. [17]. Also presented for comparison in Fig. 1 are the ''exact'' energies of Kolos and Wolniewicz [18] and the EHFACE2 [19,20] diatomic curves employed in the global H_3 DMBE potential energy surface [21]. Clearly, the agreement between the semiempirically corrected SOCI energies, the ''exact'' Kolos-Wolniewicz results and the EHFACE2 curve is good. We emphasize that the $\mathscr{F}^{(2)}$ parameters have been obtained from the requirement that the well depth of the DMBE-SEC curve should reproduce the experimental value. Similarly, $\mathscr{F}^{(3)}$ has been calibrated as in Ref. [12] from the requirement that the barrier
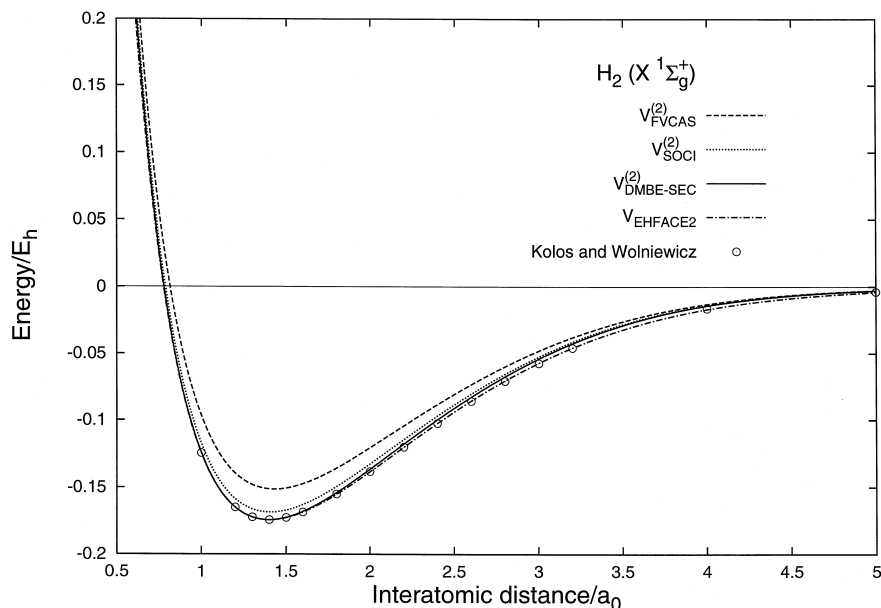

Fig. 1. Potential energy curves for H_2: solid line: DMBE-SEC (this work); dashed line: FVCAS (this work); dotted line: SOCI (this work); ⊙: Kolos-Wolniewicz (Ref. [18]); dash-dotted line: EHFACE2 (Ref. [19]).

height at the linear geometry $R_1 = R_2 = 1.757\,a_0$ reproduces the value predicted from the H_3 DMBE potential energy surface, i.e. $V_b = 9.65\,\text{kcal}\,\text{mol}^{-1}$ (without scaling, the SOCI barrier would be $V_b \sim 11.2\,\text{kcal}\,\text{mol}^{-1}$).

3. Computational method

3.1. Interfacing subroutine

A major concern in designing a subroutine to interface the dynamics and ab initio computer codes has been to write a subprogram which allows control over the electronic structure calculations, while remaining independent of the system and level of theory. Our solution has been to use a template file for each level of calculation (ROHF, FVCAS and SOCI) to produce the input file. Thus, at each level of calculation, the template file is read and a new file written based on it just by replacing the coordinates.

To write the interfacing subroutine, the following guidelines have been used:
1. the subroutine should return the DMBE-SEC energy and gradient in the framework of the appropriate coordinates;
2. the subroutine should create an input file suitable for GAMESS, while being straightforward to replace, if a different suite of programmes is utilized to carry out the ab initio calculations;
3. the subroutine should read the results of the ab initio calculations from the resulting output files;
4. the energies and gradients of the diatomic fragments should be calculated and spline fitted prior to the dynamics study to facilitate usage at any arbitrary geometry of the three-atom system;
5. no changes should be made on GAMESS, except transforming it to a subprogram;
6. the subroutine should be as simple and general as possible.

Fig. 2 shows the flowchart of the subprogram to perform the DMBE-SEC calculations, which is driven by the master dynamics code.
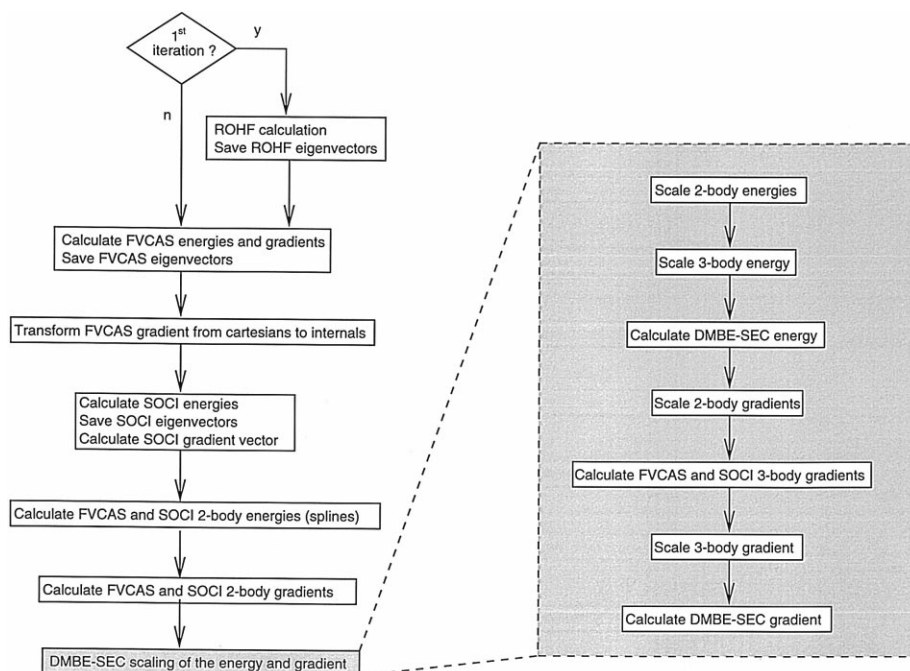
Fig. 2. Flowchart of the subprogram which performs the calculation of the energies and gradients used in the trajectory calculations.

3.2. General procedure and technical details

Following item 4 of the guidelines presented in Section 3.1, the dynamics study is preceded by calculations of the DMBE-SEC energies and gradients for the diatomic fragments. To allow their use at any point along the trajectory, such calculations are then interpolated using cubic splines.

We discuss now the various steps used to integrate a quasi-ab initio trajectory. This is initiated with a ROHF calculation to generate the starting vectors for the FVCAS calculation. Such vectors are utilized next to calculate the SOCI energy. Since GAMESS does not provide an option to calculate the gradient of a SOCI wavefunction, this has been obtained numerically using a three-point finite difference approximation. For this, the starting orbitals employed at each displaced geometry are those obtained from the SOCI energy calculation. As usual, the orbital space in the FVCAS wavefunction has been divided into the active space (three orbitals for H_3: one doubly occupied, one singly occupied and a valence orbital) and the external space. Only the orbitals that belong to the external space have been correlated at the SOCI level. It should be noted that GAMESS gives the gradients in terms of the cartesian coordinates and hence they need to be expressed in terms of the interatomic coordinates (R_1, R_2, R_3). For the conversion, we carry out a single value decomposition (SVD) decomposition of the relevant 9×3 matrix, as we describe briefly in the following. Let the cartesian coordinates for the three atoms be $A(x_1, x_2, x_3)$, $B(x_4, x_5, x_6)$ and $C(x_7, x_8, x_9)$ and define the internuclear distances as $R_1 = R_{AB}$, $R_2 = R_{BC}$, $R_3 = R_{CA}$. One obtains from the chain rule

$$\frac{\partial V}{\partial x_i} = \sum_k \frac{\partial V}{\partial R_k}\frac{\partial R_k}{\partial x_i}, \quad i = 1,\ldots,9, \quad k = 1,\ldots,3 \tag{4}$$

and, in matrix form,

$$\mathbf{g}_C = \mathbf{A}\mathbf{g}_R \tag{5}$$

where $\mathbf{g}_C$ is the gradient of the energy with respect to the cartesian coordinates, $\mathbf{g}_R$ is the gradient of the energy with respect to the interatomic coordinates

and **A** is the transformation matrix $A_{ij} = \partial R_i / \partial x_j$ which assumes the explicit form

$$\mathbf{A} = \begin{bmatrix} -\dfrac{x_4 - x_1}{R_1} & 0 & \dfrac{x_1 - x_7}{R_3} \\[2mm] -\dfrac{x_5 - x_2}{R_1} & 0 & \dfrac{x_2 - x_8}{R_3} \\[2mm] -\dfrac{x_6 - x_3}{R_1} & 0 & \dfrac{x_3 - x_9}{R_3} \\[2mm] \dfrac{x_4 - x_1}{R_1} & -\dfrac{x_7 - x_4}{R_2} & 0 \\[2mm] \dfrac{x_5 - x_2}{R_1} & -\dfrac{x_8 - x_5}{R_2} & 0 \\[2mm] \dfrac{x_6 - x_3}{R_1} & -\dfrac{x_9 - x_6}{R_2} & 0 \\[2mm] 0 & \dfrac{x_7 - x_4}{R_2} & -\dfrac{x_1 - x_7}{R_3} \\[2mm] 0 & \dfrac{x_8 - x_5}{R_2} & -\dfrac{x_2 - x_8}{R_3} \\[2mm] 0 & \dfrac{x_9 - x_6}{R_2} & -\dfrac{x_3 - x_9}{R_3} \end{bmatrix} \tag{6}$$

Since **A** is a rectangular matrix (the linear system of equations has more equations than unknowns), a SVD procedure must be used to obtain the gradient in terms of the interatomic distances by solving Eq. (5). To conclude, we emphasize that GAMESS has been employed in all ab initio electronic structure calculations together with the standard 6-311G(d,p) basis set of Krishnan et al. [17]. This has been found to be about the smallest possible, capable of yielding a SEC curve for H_2 in good agreement with the 'exact' data of Kolos and Wolniewicz [18] away from the minimum.

4. Results and discussion

Calculations have been carried for the reaction $H + H_2(v,j) \rightarrow H_2(v',j') + H$ at a fixed translational energy of 55.35 kcal mol^{-1}. The H_2 molecule

has been kept in its ground vibrational-rotational state ($v = j = 0$) and the initial atom-diatom separation fixed at $6.5\,a_0$, a sufficiently large value to warrant that the interaction energy between the hydrogen atom and the H_2 molecule is small. In turn, the integration step size has been fixed at 2.0 au and the maximum impact parameter at $b_{max} = 2.6\,a_0$. Such parameters have been optimized from conventional trajectory calculations carried out on the H_3 DMBE potential energy surface. Although this procedure has been employed here for convenience, those parameters could have been instead obtained by running trajectories 'on-the-fly'. All other initial conditions have been sampled in the standard manner [22].

The reactive cross section is given by

$$\sigma_r = \pi\, b_{max}^2\, P_r \tag{7}$$

where $P_r = N_r/N$ is the reactive probability and the associated 68% error interval is

$$\Delta\sigma_r = \left[\frac{N - N_r}{N N_r}\right]^{1/2} \sigma_r \tag{8}$$

Table 1 summarizes the trajectory results at various stages of the present computations, namely after running a total of 120, 170 and 304 trajectories. Also given for comparison in the last entry of Table 1 is the reactive cross section computed by running a total of 3281 trajectories on the DMBE potential energy surface, a value which is about 11 times larger than the maximum number of trajectories considered for the quasi- ab initio dynamics calculations of the present work. Note that $\langle v'_r \rangle$ denotes the average product vibrational quantum number obtained from the reactive trajectories, while $\langle v' \rangle$ denotes the corresponding value when the whole set of trajectories (reactive and non-reactive) is considered. A similar meaning is implied for the rotational quantum number in the products ($\langle j'_r \rangle$ and $\langle j' \rangle$, respectively). Two salient features are apparent. First, the 'on-the-fly' dynamics calculations are seen to lead essentially to the same dynamical attributes as those based on the accurate H_3 DMBE potential energy surface. Indeed, only $\sim 1\%$ of the total number of trajectories yielded different outcomes. Second, the results appear to be moderately converged after 200 trajectories or so. Of course, such a number of

trajectories is affordable for many systems of practical interest which, like the present one, involve a potential energy barrier, while being probably sufficient in general to get reasonable estimates of the reactive cross section for not too low translational energies.

Fig. 3 illustrates a typical 'on-the-fly' reactive trajectory for the title reaction. This shows excellent agreement with the conventional trajectory run on the global H_3 DMBE potential energy surface for the same initial conditions. In fact, a close examination shows that the 'on-the-fly' and conventional trajectories are in almost perfect agreement with each other at each integration point (there are typically about one thousand such points) and hence we omit the latter for clarity in Fig. 3. For the few divergent trajectories mentioned above, the agreement between the 'on-the-fly' and conventional tra-

Table 1
A summary of the trajectory calculations

Quantities		DMBE	DMBE-SEC
N		120	120
	$\langle v' \rangle$	0.09	0.09
	$\langle j' \rangle$	4.54	4.84
N_r		40	37
	$\langle v'_r \rangle$	0.23	0.24
	$\langle j'_r \rangle$	8.98	9.19
σ^r		7.08 ± 0.91	6.55 ± 0.90
N		170	170
	$\langle v' \rangle$	0.09	0.09
	$\langle j' \rangle$	4.60	4.79
N_r		62	59
	$\langle v'_r \rangle$	0.21	0.18
	$\langle j'_r \rangle$	8.81	8.88
σ^r		7.70 ± 0.78	7.33 ± 0.77
N		304	304
	$\langle v' \rangle$	0.10	0.09
	$\langle j' \rangle$	4.60	4.89
N_r		107	105
	$\langle v'_r \rangle$	0.21	0.19
	$\langle j'_r \rangle$	9.20	9.26
σ^r		7.47 ± 0.58	7.34 ± 0.58
		6.60 ± 0.18[a]	

All symbols have their meaning assigned in the text. The reactive cross section σ^r is in atomic units. [a] Value obtained by running a total of 3281 trajectories on the DMBE [21] potential energy surface.
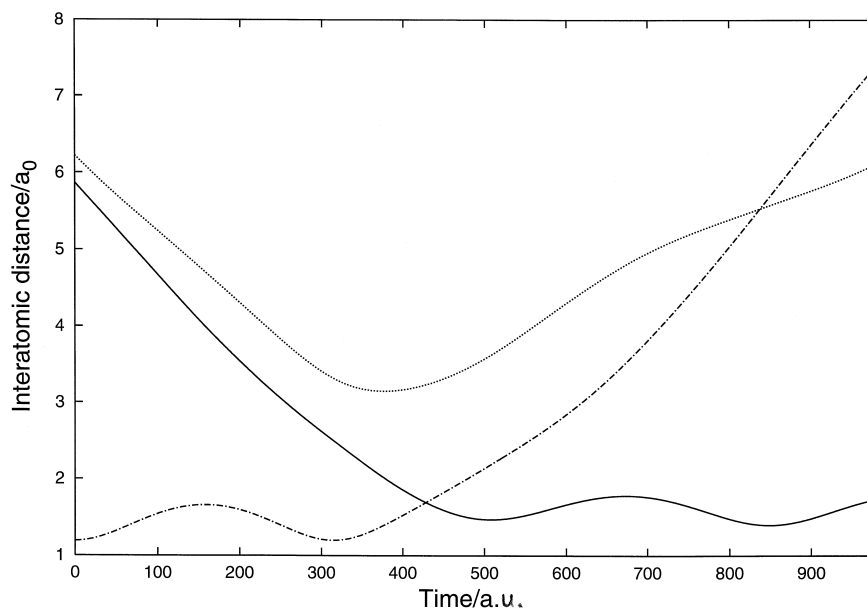
Fig. 3. Distance vs. time plot for a typical 'on-the-fly' $H + H_2$ reactive trajectory run using the DMBE-SEC energies and gradients. Distinct lines are used to indicate the three interatomic distances.

jectories is excellent only for the initial part of the trajectory. From a break-up point onwards they diverge seriously, which can be tentatively attributed to some exponential divergence caused by traversing a chaotic region of the potential energy surface. Of

course, any subtle differences between the DMBE-SEC and the analytical DMBE potential energy surfaces may also be responsible for such a divergence.

Fig. 4 illustrates the error in conserving the total energy, which is, of course, a first integral of the
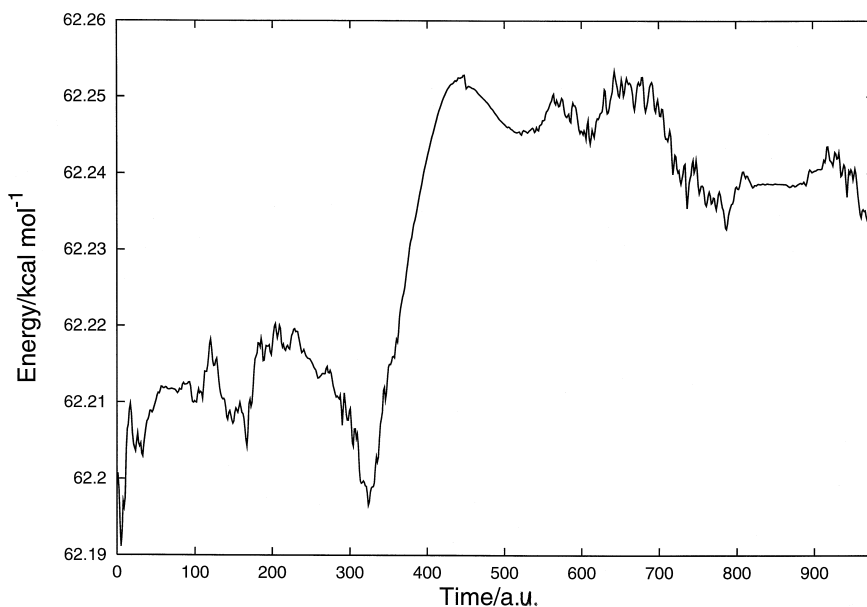

Fig. 4. Total energy vs. time plot for the 'on-the-fly' trajectory shown in Fig. 3.

motion. Clearly, the numerical errors amount typically to 10^{-2} kcal mol^{-1}, a value which has been found tolerable to mimic the energy partition in the products when the integration is carried out using the DMBE potential energy surface to simulate the ab initio energies and gradients. Of course, arbitrary accuracy may in principle be achieved by varying the integration step size, although this is done at the expense of an increased computational cost.

5. Concluding remarks

We have suggested a method for calculating quasiclassical trajectories 'on-the-fly' using relatively inexpensive SOCI electronic structure calculations. To account for the unavoidable errors due to the truncation of the configuration-interaction expansion and incompleteness of the one-electron basis sets, the external correlation energy has been scaled using the DMBE-SEC [12] method. The traditional approach to integrate the trajectories has been used, with the energy and its gradient at the various levels of ab initio theory being calculated using the GAMESS suite of programs suitably adapted to be driven as a subprogram by the dynamics code. In principle, the trajectories can be computed to arbitrary accuracy by varying the integration step size. Test results for the $H + H_2$ exchange reaction have been shown to be in excellent agreement with those obtained from traditional QCT calculations using the accurate H_3 DMBE potential energy surface. A final comment concerns the computational cost. For the translational energy and integration step size considered in present work, each trajectory costs typically 9 hours of CPU time on an Alpha 600 workstation available at the Theoretical & Computational Chemistry group. Of course, one expects that the efficiency of the method can be greatly improved by using parallel computing strategies in which different trajectories can be handled by distinct processors. Moreover, the calculation of the gradient (and Hessian in case one wishes to use the QCT/GH method described in Ref. [8]) can take advantage of parallelization, since analytical derivatives are not available yet for some electronic correlated methods frequently employed in reaction dynamics. In addition, by combining the trajectory calculations with available interpolation schemes (Refs. [23] and [24], and references therein) one may

generate a portion of the full potential energy surface which may then be used for other purposes, e.g. quantum dynamics calculations. Although straightforward to implement, no attempt has been made here to constrain the classical energy of a bound vibrational mode to be larger than the zero-point value. The above are topics that we plan to explore in future work.

Although we had to give the technical details on the implementation of the computer algorithm, we would not like to conclude without pointing out that the aspects raised here have aimed to go much beyond such technicalities. In fact the major message, which is simple but yet often overlooked, lies at the very heart of the theory of chemical physics. It points out that brute force ab initio calculations coupled to a molecular dynamics code can lead at present to a prohibitive route towards ''on-the-fly'' studies of collisional processes. A much more successful way may be that suggested in the present work which is based on the linear scaling of the *n*-body dynamical correlation energies that are calculated from fairly modest (on current ab initio standards) SOCI wavefunctions. This has been here clearly demonstrated for the case of the $H + H_2$ reaction which has long provided a testing ground for theoretical reaction dynamicists. In summary, the simplicity of our approach and the expected progresses in computing sciences will probably make it competitive with the traditional one in the future. Indeed, obtaining an accurate global potential energy surface is a difficult problem, even for a triatomic molecule.

Acknowledgements

References

[1] P. Pulay, in: Ab Initio Methods in Quantum Chemistry – II, ed. K.P. Lawley (Wiley, New York, 1987) p. 241.
[2] N.C. Handy, J.F. Gaw, E.D. Simandiras, J. Chem. Soc., Faraday Trans. 2 (1987) 83 1577.

[3] T. Helgaker, P. Jorgensen, Adv. Quant. Chem. 19 (1988) 183.

[4] A.J.C. Varandas, Adv. Chem. Phys. 74 (1988) 255.

[5] A.J.C. Varandas, A.I. Voronin, Mol. Phys. 95 (1995) 497.

[6] T. Helgaker, E. Uggerud, H.J.Aa. Jensen, Chem. Phys. Lett. 173 (1990) 145.

[7] K.D. Gibson, H.A. Scheraga, J. Comput. Chem. 11 (1990) 468.

[8] A.J.C. Varandas, J.M.C. Marques, J. Chem. Phys. 100 (1994) 1908.

[9] S.L. Mielke, G.C. Lynch, D.G. Truhlar, D.W. Schwenke, J. Phys. Chem. 98 (1994) 8000.

[10] K.F. Lim, J. Chem. Soc. Faraday Trans. 93 (1997) 669.

[11] M.W. Schmidt, K.K. Baldridge, J.A. Boatz, S.T. Elbert, M.S. Gordon, J.H. Jensen, S. Koseki, N. Matsunaga, K.A. Nguyen, S.J. Su, T.L. Windus, M. Dupuis, J.A. Montgomery, J. Comput. Chem. 14 (1993) 1347.

[12] A.J.C. Varandas, J. Chem. Phys. 90 (1989) 4379.

[13] A.J.C. Varandas, in: Trends in Atomic and Molecular Physics, ed. M. Yáñez (Universidad Autonoma de Madrid, Madrid, 1990) p. 113.

[14] P. Jimeno, J.C. Rayez, P.E. Abreu, A.J.C. Varandas, J. Phys. Chem. 101 (1997) 4828.

[15] F.B. Brown, D.G. Truhlar, Chem. Phys. Lett. 117 (1985) 307.

[16] J. Simons, J. Phys. Chem. 93 (1989) 626.

[17] R. Krishnan, J.S. Binkley, J.A. Pople, J. Chem. Phys. 72 (1980) 650.

[18] W. Kolos, L. Wolniewicz, Chem. Phys. Lett. 24 (1974) 457.

[19] A.J.C. Varandas, J.D. Silva, J. Chem. Soc., Faraday Trans. 2 (1986) 82 593.

[20] A.J.C. Varandas, J.D. Silva, J. Chem. Soc. Faraday Trans. 88 (1992) 941.

[21] A.J.C. Varandas, F.B. Brown, C.A. Mead, D.G. Truhlar, N.C. Blais, J. Chem. Phys. 86 (1987) 6258.

[22] D.G. Truhlar, J.T. Muckerman, in: Atom-Molecule collision theory, ed. R.B. Bernstein (Plenum, New York, 1979) p. 505.

[23] T. Ishida, G.C. Schatz, J. Chem. Phys. 107 (1997) 3558.

[24] M.A. Collins, Adv. Chem. Phys. 93 (1996) 389.