Semi-classical correction for quantum-mechanical scattering

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Abstract

A straightforward theoretical prescription is described for combining any approximate quantum scattering calculation with a semi-classical correction. The correction involves the standard semi-classical approximation to the time evolution operator, so that only real time trajectories are needed; by transforming to an initial value representation the calculations require only an average over the phase space of initial conditions. To the extent that the semi-classical approximation is accurate, the net result for the S matrix is exact. Application to one-dimensional barrier transmission shows the semi-classical approximation to do a very good job, for energies above, near to, or far below the barrier.

1. Introduction

The last few years have seen quite significant advances in rigorous quantum-mechanical calculations for the dynamics of simple chemical reactions [1–4]. This is due both to new developments in theoretical methodology and to continued increases in computational power. To date the most complex reaction that has been described rigorously (i.e. in its full dimensionality, six degrees of freedom) is [5] $H_2+OH \rightarrow H+H_2O$. Computers will of course continue to increase in speed and memory size, making it possible to extend these rigorous approaches to more complex (i.e. larger) molecular systems, but it is clear that one will always be interested in carrying out reliable calculations that are beyond the capability of a fully rigorous quantum treatment.

One strategy for dealing with more complex systems is to employ a hybrid approach, one that combines an accurate quantum treatment of the few (<6, say) degrees of freedom that are most important in a given reaction with a more approximate treatment of

the (perhaps many) remaining degrees of freedom that play a more passive role. An attractive candidate for the "more approximate" way of dealing with the many passive degrees of freedom is classical (or semi-classical) mechanics, for it is well recognized that classical trajectory simulations are feasible for truly complex molecular systems. The idea, therefore, is to combine an accurate quantum description of a few degrees of freedom with a classical (or semi-classical) treatment of everything else. Feynman path integral methods [6,7] offer one approach for devising methods of this type, as does the time-dependent self-consistent field (TD-SCF) method [8–11].

This paper describes another approach for combining an approximate quantum description with a semi-classical approximation, one based on time-independent scattering theory. Section 2 describes the basic theoretical ideas, and section 3 presents the results of a simple but not totally trivial test problem, testing how well the semi-classical approximation describes barrier transmission (the one-dimensional model of a chemical reaction). The results for this

test problem are extremely encouraging, convincing us that this approach is worthy of further development for interesting applications.

2. Overview of the theory

The most complete characterization of a bimolecular scattering process (reactive or nonreactive) is the S matrix, in terms of which all reaction probabilities, cross sections, rate constants, etc., can be expressed. A formally exact expression for the S matrix elements is

$$S_{n_p,n_r}(E) = S^0_{n_p,n_r}(E) + (i/\hbar)[\langle \Phi_{n_p} | (\hat{H}-E| \Phi_{n_r} \rangle$$

$$+ \langle \chi_{n_p} | \hat{G}^+(E) | \chi_{n_r} \rangle] , \quad (1)$$

where

$$\chi_{n_r} \equiv (\hat{H}-E)\Phi_{n_r} , \quad (2a)$$

$$\chi_{n_p} \equiv (\hat{H}-E)\Phi_{n_p} , \quad (2b)$$

and n_p, n_r denote the product and reactant quantum numbers, respectively. $\hat{H}$ is the total Hamiltonian and $G^+(E)$ the full Green function for the problem. Φ_n is any (regular) scattering wavefunction with a unit incoming wave in channel n and outgoing waves in all other open channels n'; i.e. the asymptotic form for Φ_n for large R is

$$\Phi_n(r, R) \approx -\phi_n(r) \frac{\exp(-ik_n R)}{\sqrt{v_n}}$$

$$+ \sum_{n'} \phi_{n'}(r) \frac{\exp(ik_{n'} R)}{\sqrt{v_{n'}}} S^0_{n',n} , \quad (3)$$

where R denotes the coordinate for relative translation of the two colliding molecules and r the remaining (internal) coordinates of the system. $\{\phi_n(r)\}$ and v_n are the eigenfunction and translational velocity for the nth channel, respectively.

Eqs. (1)–(2) are essentially the distorted wave representation [12] of the S matrix; it is formally exact for whatever "distorted waves" one uses for the Φ's. Note that we are using the convention that wavefunction in the bra symbol $\langle |$ are *not* complex conjugated. This is a carry over from using this convention in quantum scattering calculations via the S matrix Kohn variational method [13,14] and is useful because it more explicitly reveals the symmetry of

the S matrix. The specific form and normalization used for the Φs is also carried over from this earlier work.

In fact, one may recognize that the first two terms of Eq. (1) are the S-matrix Kohn variational functional [14] itself,

$$S^{KVP}_{n_p,n_r} \equiv S^{DWBA}_{n_p,n_r} \equiv S^0_{n_p,n_r}$$

$$+ (i/\hbar) \langle \Phi_{n_p} | (\hat{H}-E) | \Phi_{n_r} \rangle , \quad (4a)$$

which we have also noted is the distorted wave Born approximation [12] (DWBA) (i.e. the Kohn variational method is the DWBA where the distorted waves are chosen variationally). It is thus useful to write Eq. (1) as

$$S_{n_p,n_r} = S^{DWBA}_{n_p,n_r} + \Delta S_{n_p,n_r} , \quad (4b)$$

where $\Delta S_{n_p,n_r}$ is the third term in eq. (1),

$$\Delta S_{n_p,n_r} = (i/\hbar) \langle \chi_{n_p} | \hat{G}^+(E) | \chi_{n_r} \rangle , \quad (4c)$$

which contains all higher-order corrections beyond the DWBA/KVP. In the Kohn variational method one takes the Φs to be a linear combination of a given basis set and chooses the expansion coefficients by making Eq. (4a) stationary; if the basis is large enough, the correction term $\Delta S_{n_p,n_r}$ will be negligible (because $\chi \equiv (H-E)\Phi$ will be approximately zero), but for sufficiently large molecular systems this will not be possible.

One can imagine other ways of choosing approximate scattering wavefunctions for the Φs. The one which accomplishes the purposes discussed in section 1 would be a "reduced dimensionality" [15] wavefunction; i.e. one would carry out a quantum scattering calculation for the few most important degrees of freedom, assuming the others to be uncoupled from them (or perhaps training them within a vibrationally adiabatic approximation). $S^{DWBA}_{n_p,n_r}$ would thus be an accurate quantum-mechanical result involving the few important degrees of freedom, with the correction to this, $\Delta S_{n_p,n_r}$, to be approximated semi-classically (vide infra).

We refer to Eq. (1), or Eq. (4), as *formally* exact because the correction term, Eq. (4c), involves the full Green function, the construction of which is tantamount to solving the full Schrödinger equation (with boundary conditions Eq. (3)). Thus in any practical calculation one must approximate this term,

and herein lies the semi-classical approximation. Using the exact relation

$$G^+(E) = \frac{1}{i\hbar} \int\limits_0^\infty dt \, \exp(iEt/\hbar) \, \exp(-i\hat{H}t/\hbar) \qquad (5)$$

and the standard (Van Vleck–Gutzwiller [16,17]) semi-classical approximation for the time evolution operator, the semi-classical approximation to the correction term is

$$\Delta S_{n_\mathrm{p}, n_\mathrm{r}}^{\mathrm{sc}} = \frac{1}{\hbar^2} \frac{1}{(2\pi i\hbar)^{F/2}}$$

$$\times \sum_\alpha \int d\boldsymbol{q}_2 \int d\boldsymbol{q}_1 \int\limits_0^\infty dt \left| \mathrm{Det}\left(\frac{\partial \boldsymbol{q}_2(\boldsymbol{q}_1, \boldsymbol{p}_1; t)}{\partial \boldsymbol{p}_1} \right) \right|^{-1/2}$$

$$\times \chi_{n_\mathrm{p}}(\boldsymbol{q}_2) \exp\left(\frac{i(\mathscr{S}_\alpha(\boldsymbol{q}_2, \boldsymbol{q}_1; t) + Et)}{\hbar} - \frac{i\pi\mu_\alpha}{2} \right)$$

$$\times \chi_{n_\mathrm{r}}(\boldsymbol{q}_1) , \qquad (6)$$

where $\mathscr{S}_\alpha(\boldsymbol{q}_2, \boldsymbol{q}_1; t)$ is the classical action for the αth trajectory that goes from $\boldsymbol{q}_1$ at time $t=0$ to $\boldsymbol{q}_2$ at time t,

$$\mathscr{S}_\alpha(\boldsymbol{q}_2, \boldsymbol{q}_1; t) = \int\limits_0^t dt' \, [\boldsymbol{p}(t') \cdot \dot{\boldsymbol{q}}(t')$$

$$- H(\boldsymbol{p}(t'), \boldsymbol{q}(t'))] , \qquad (7)$$

and the sum over α is over all possible trajectories that satisfy this double ended boundary condition. μ_α in Eq. (6) is the Maslov index [18], the number of zeros experienced by the Jacobian determinant in the time interval $(0, t)$. (Note also that it has been assumed in Eqs. (6) and (7) that the Hamiltonian is of Cartesian form.)

The evaluation of Eq. (6) is greatly simplified by the transformation to an initial value representation [19,20]; i.e. for fixed $\boldsymbol{q}_1$ and t, one changes integration variable from $\boldsymbol{q}_2$ to $\boldsymbol{p}_1$,

$$\sum_\alpha d\boldsymbol{q}_2 \equiv \left| \mathrm{Det}\left(\frac{\partial \boldsymbol{q}_2(\boldsymbol{q}_1, \boldsymbol{p}_1; t)}{\partial \boldsymbol{p}_1} \right) \right| d\boldsymbol{p}_1 , \qquad (8)$$

where we have emphasized that the sum over multiple trajectories is subsumed in the integration over $\boldsymbol{p}_1$ because initial conditions $(\boldsymbol{p}_1, \boldsymbol{q}_1)$ determine a unique classical trajectory. Eq. (6) thus becomes

$$\Delta S_{n_\mathrm{p}, n_\mathrm{r}}^{\mathrm{sc}} = \frac{1}{\hbar^2} \frac{1}{(2\pi i\hbar)^{F/2}}$$

$$\times \int d\boldsymbol{p}_1 \int d\boldsymbol{q}_1 \int\limits_0^\infty dt \left| \mathrm{Det}\left(\frac{\partial \boldsymbol{q}_2(\boldsymbol{q}_1, \boldsymbol{p}_1; t)}{\partial \boldsymbol{p}_1} \right) \right|^{1/2}$$

$$\times \chi_{n_\mathrm{p}}(\boldsymbol{q}_2) \exp\left(\frac{i(\mathscr{S}(\boldsymbol{q}_2, \boldsymbol{q}_1; t) + Et)}{\hbar} - \frac{i\pi\mu}{2} \right)$$

$$\times \chi_{n_\mathrm{r}}(\boldsymbol{q}_1) , \qquad (9)$$

where $\boldsymbol{q}_2 = \boldsymbol{q}_2(\boldsymbol{q}_1, \boldsymbol{p}_1; t)$. Eq. (9) thus involves an integral over the phase space of initial conditions. (The integral over time t in Eq. (9) can be carried out as one is computing the trajectory.)

The classical S-matrix theory [19–21] developed in the early 1970s can be viewed as the stationary phase approximation for evaluating all the integrals in Eq. (6) or (9), but here we wish to evaluate them exactly (numerically) [*1]. Our interest in this has been spurred by Heller's recent work [22–26] showing that this "primitive" semi-classical approximation can be surprisingly accurate, even for long times and in situations where the classical mechanics is chaotic. In Eq. (9) we expect that only relatively short time dynamics will be required – because the functions $\chi_{n_\mathrm{r}}(\boldsymbol{q}_1)$ and $\chi_{n_\mathrm{p}}(\boldsymbol{q}_2)$ decay rapidly (as $\mathscr{L}^2$ functions) for large $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ – so that the semi-classical approximation has an even better chance of being usefully accurate. To the extent that the semi-classical approximation for $\Delta S_{n_\mathrm{p}, n_\mathrm{r}}$ is accurate, the net result, Eq. (4b), will be invariant to the choice of the approximate wavefunctions $\{\Phi_n\}$. The more closely the Φs approximate the complete solution of the Scrhödinger equation, then of course the smaller will be the semi-classical correction term.

3. Application to a one-dimensional barrier

Here we test the ideas of section 2 on a one-dimensional model of a chemical reaction, namely trans-

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[*1] Though the stationary phase approximation introduces no additional error beyond that already inherent in the semi-classical propagator (error of order $\hbar$), in practice things may be quite different. For example, if the potential function is quadratic – i.e. harmonic oscillators or parabolic barriers – the semi-classical approximation to the propagator $\langle q_2 | \exp(-iHt/\hbar) | q_1 \rangle$ happens to be *exact*. In this case Eq. (6) and (9) are exact if the integrals are evaluated exactly, while the stationary phase approximation introduces error of order $\hbar$.

mission through an Eckart barrier [27],

$$V(q) = V_0 \operatorname{sech}^2(\alpha q) . \tag{10}$$

The barrier height, V_0, and the mass, m, were chosen to be 0.425 eV and 1060 au, respectively. α is set equal to 1.3624 au. With this choice of parameters, the potential approximately corresponds to the collinear $H + H_2$ reaction.

To provide the most stringent test of the semi-classical approximation we make the simplest possible choice for the wavefunctions $\{\Phi_n\}$, smoothly cutoff plane waves (with reactants r to the left, products p to the right),

$$\Phi_{n_r}(q) = \frac{1}{\sqrt{v}} \exp(ikq) \, h(-q-a) , \tag{11a}$$

$$\Phi_{n_p}(q) = \frac{1}{\sqrt{v}} \exp(-ikq) \, h(q-a) , \tag{11b}$$

where $h(\eta)$ is a smooth step function ($= 1$ for $\eta \gg 0$, and 0 for $\eta \ll 0$). For the applications below we used the particular function

$$h(\eta) = \frac{1}{1 + e^{-\lambda \eta}} . \tag{12}$$

Thus $\Phi_{n_r}(q)$ is cutoff smoothly on the left (reactant) side of the barrier at $q \approx -a$, so that

$$\Phi_{n_r}(q) \approx \frac{1}{\sqrt{v}} \exp(ikq) , \quad \text{for } q \ll -a ,$$

$$\Phi_{n_r}(q) \approx 0 , \quad \text{for } q \gg -a ,$$

and similarly for $\Phi_{n_p}(q)$ at $q \approx +a$. The zeroth-order term in Eq. (1) (and (4a)) is thus zero, so that

$$S^{\mathrm{DWBA}}(E) = \frac{i}{\hbar} \langle \Phi_{n_p} | (H-E) | \Phi_{n_r} \rangle , \tag{13}$$

which with the particular Φs of Eq. (11) is given by

$$S^{\mathrm{DWBA}}(E) = \frac{i}{\hbar v} \int_{-\infty}^{\infty} \mathrm{d}q \, [V(q)h_p h_r$$

$$+ i\hbar v h_p \delta_r - \frac{\hbar^2}{2m} \delta_p \delta_r] , \tag{14}$$

where

$$h_r \equiv h(-q-a) , \quad h_p \equiv h(q-a) ,$$

$$\delta_r \equiv \delta(q+a) , \quad \delta_p \equiv \delta(q-a) .$$

$\delta(\eta) \equiv h'(\eta)$ is a smooth pre-limit version of a Dirac delta function; with Eq. (3) for $h(\eta)$, one has

$$\delta(\eta) = \tfrac{1}{4}\lambda \operatorname{sech}^2(\tfrac{1}{2}\lambda\eta) . \tag{15}$$

The explicit form of the semi-classical correction term is

$$\Delta S^{\mathrm{sc}}(E) = \frac{1}{\hbar^2 v}$$

$$\times \int_{-\infty}^{\infty} \mathrm{d}q_1 \int_{-\infty}^{\infty} \mathrm{d}p_1 \int_0^{\infty} \mathrm{d}t \, \mathscr{F}(q_1, p_1, t)$$

$$\times \exp[(i/\hbar)\gamma(q_1, p_1, t)] , \tag{16}$$

where

$$\gamma \equiv \hbar k[q_1 - q_2(q_1, p_1, t)] + Et$$

$$+ \mathscr{S}(q_1, p_1, t) - \tfrac{1}{2}i\pi\hbar(\mu + \tfrac{1}{2}) , \tag{17}$$

$$\mathscr{F} \equiv \left(\frac{1}{2\pi\hbar} \left| \frac{\partial q_2}{\partial p_1} \right| \right)^{1/2} \left[V(q_1)h_r + \frac{i\hbar}{2}\left(v + \frac{p_1}{m}\right)\delta_r \right]$$

$$\times \left[V(q_2)h_p + \frac{i\hbar}{2}\left(v + \frac{p_2}{m}\right)\delta_p \right] , \tag{18}$$

where $q_2 = q_2(q_1, p_1; t)$, $p_2 = p_2(q_1, p_1; t)$, and $v = \sqrt{2E/m}$. The integral over t in Eq. (16) is evaluated simultaneously with computing the trajectory with initial conditions (p_1, q_1). The integral over q_1 is well behaved, and though that over p_1 is less so, it can be handled with appropriate care.

Fig. 1 shows the transmission probability $P(E) \equiv |S(E)|^2$ as a function of energy for the cutoff parameter $a = 5 \ a_0$. This corresponds to cutting off the Φs well into their respective asymptotic regions, and in this case one can see that variational term in Eq. (14) is essentially zero (because Φ_{n_r} and Φ_{n_p} have no overlap). Thus the entire contribution to the transmission probability is from the semiclassical correction term in Eq. (16), and it is impressive to see how well it does even in the deep tunneling region. For transmission probabilities below 10^{-6} it becomes progressively worse, being about an order of magnitude too large when $P \approx 10^{-7}$.

Note that all the trajectories that contribute in Eq. (16) go from $q_1 \leqslant -a$ to $q_2 \geqslant +a$ in real time t. They thus all have a classical energy $p_1^2/2m + V(q_1)$ that lies *above* the barrier, even though the energy E may be above or below the barrier. Were E below the bar-
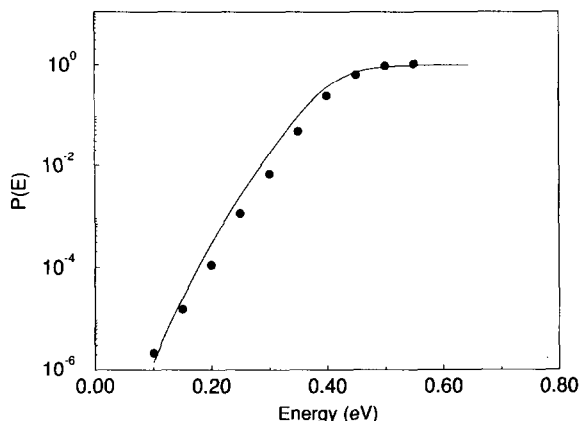
Fig. 1. Transmission probability, $P(E)$, as a function of total energy. The cutoff parameters are, $\lambda = 2.5$ au and $a = 5.0$ au. Solid line is the exact result, and the points correspond to the present semi-classical results.
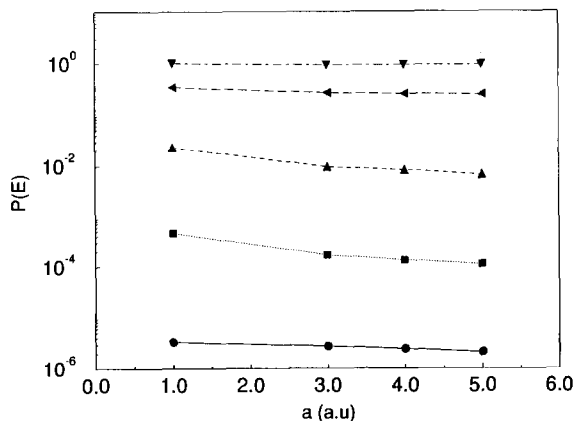

Fig. 2. Variation in $P(E)$ as a function of the cutoff parameter a with λ fixed at 2.5 au. (●) $E = 0.1$ eV, (■) $E = 0.2$ eV, (▲) $E = 0.3$ eV, (◄) $E = 0.4$ eV and (▼) $E = 0.5$ eV.

rier and the integral over t evaluated by the stationery phase approximation, the stationary value of t would be *complex* and the corresponding classical trajectory would have energy E. Thus whether the classical trajectories go *over* the barrier (real time) or tunnel *through* the barrier (complex time) is simply a matter of how one does the time integral. See ref. [20] for a more complete discussion of this point.

Fig. 2. shows how the transmission probabilities vary as a function of the cutoff parameter a, for several representative values of energy E. If the semi-classical approximation were exact, $P(E)$ would be

independent of the parameter a (and of the particular choice of "distorted waves" Φ_{n_r} and Φ_{n_p} in general), so the stability of the result with respect to variations of this parameter is an indication of the robustness of the semi-classical approximation. Fig. 2 shows that over the entire range of energy, from above to far below the top of the barrier, the transmission probability varies only modestly over a wide range of values of the cutoff parameter.

4. Concluding remarks

The theoretical approach in section 2 shows a very straight forward procedure for combining an approximate quantum-mechanical treatment of a scattering process with a semi-classical theory which corrects (approximately) for the lack of completeness of the quantum treatment. The example in section 3 shows that the semi-classical approximation does quite a good job of describing one-dimensional barrier transmission, even in the deep tunneling region, and even when the quantum wavefunctions are the simplest ones possible (plane waves). One would clearly expect the results to be even more accurate if better wavefunctions (i.e. distorted waves) were used. However, we believe that the greatest potential of this approach is for multidimensional problems. The distorted waves can be chosen to be the scattering wavefunctions that describe a few (of the most important) degrees of freedom accurately; i.e. what *can* be done accurately quantum mechanically *should* so be done. The semi-classical approximation is then only needed to correct for the couplings between the various degrees of freedom that are omitted in the quantum wavefunctions. The utility of these ideas, however, must be demonstrated by substantive applications.

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6. References

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