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Recent Developments in the Quantum Mechanical Theory of Chemical Reaction Rates

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RECENT DEVELOPMENTS IN THE QUANTUM MECHANICAL THEORY OF CHEMICAL REACTION RATES

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Abstract

As one tries to construct an increasingly rigorous quantum mechanical generalization of classical transition state theory, one that is free of all "extraneous" approximations (e.g., separability of a one dimensional reaction coordinate), one is ultimately driven to the dynamically exact quantum treatment. Though it seems pointless to call this a transition state "theory" (it is in effect a quantum mechanical simulation), it is nevertheless possible using transition state-like ideas to cast a fully rigorous quantum approach in a form that allows one to carry out such calculations without having to solve the complete state-to-state quantum reactive scattering problem. Rigorous calculations for the reactions $H+H_2 \rightarrow H_2+H$, $H+O_2 \rightarrow OH+O$, and $H+H_2O \rightarrow H_2+OH$ illustrate this approach. At the semiclassical level, there does exist a version of transition state theory — based on the locally 'good' action variables about the saddle point on the potential energy surface — which includes non-separable coupling between all degrees of freedom (including the reaction coordinate) in a unified manner.

Introduction

The transition state theory (TST)[1] of chemical reactions is of enormous utility in understanding and estimating the rates of chemical reactions. The fundamental dynamical assumption[2] that leads to TST, however — i.e., that the dynamics is "direct", that no trajectories cross a dividing surface more than once (*vide infra*) — is based inherently on classical mechanics, and it is not possible to quantize TST without introducing additional approximations (e.g., separability of a one dimensional reaction coordinate). As one tries to rid a quantum version of TST of all these "additional approximations" — e.g., by introducing a rigorous multidimensional tunneling correction — one is driven ultimately[3] to an *exact* quantum treatment of the reaction dynamics which is no longer a transition state "theory" (i.e., approximation).

The purpose of this paper is to review the notions alluded to above and to survey some very recent developments[4] in the rigorous quantum treatment of reactive rates. In this recent work one is able to determine the rate exactly without the necessity of a complete state-to-state reactive scattering calculation; one does not avoid having to solve the Schrödinger equation, but needs only to solve it locally, in the transition state region where the reaction dynamics is determined. The classical description of reaction rates is reviewed first, and the transition state approximation, and then the rigorous quantum treatment.

Classical Rate Theory

Figure 1 shows a schematic depiction of the potential energy surface for a generic bimolecular reaction. Within the realm of classical mechanics the thermal, or equilibrium (i.e., reactants in a Boltzmann distribution) rate constant is given by[1,3,5]

$$k(T) = Q_r(T)^{-1}\,(2\pi\hbar)^{-F} \int d\mathbf{p} \int d\mathbf{q}\; e^{-\beta H(\mathbf{p},\mathbf{q})}\, F(\mathbf{p},\mathbf{q})\, \chi_r(\mathbf{p},\mathbf{q})\,, \qquad (1)$$

where $\beta = (kT)^{-1}$, Q_r is the reactant partition function (per unit volume), H is the classical

Hamiltonian for the complete molecular system, F is a flux factor, and χ_r is the *characteristic function for reaction*. The flux factor is defined in terms of a *dividing surface*, defined by the equation

$$f(\mathbf{q}) = 0 \,, \tag{2}$$

which separates reactants (for which $f(\mathbf{q})<0$) and products (for which $f(\mathbf{q})>0$); the flux is then

$$F(\mathbf{p},\mathbf{q}) = \frac{d}{dt}\, h[f(\mathbf{q})] \,, \tag{3}$$

where h is the usual Heaviside function

$$h(\xi) = \begin{Bmatrix} 1, \xi>0 \\ 0, \xi< 0 \end{Bmatrix} . \tag{4}$$

Assuming for simplicity that the coordinates and momenta $(\mathbf{q},\mathbf{p})$ are Cartesian — so that the Hamiltonian is of the form

$$H(\mathbf{p},\mathbf{q}) = \frac{\mathbf{p}^2}{2m}\, V(\mathbf{p},\mathbf{q}) \,, \tag{5}$$

Eq. (3) for the flux becomes.

$$F(\mathbf{p},\mathbf{q}) = \delta[f(\mathbf{q})]\, \frac{\partial f}{\partial \mathbf{q}} \bullet \mathbf{p}/m \,, \tag{6}$$

where we here used the fact that $h'(\xi) = \delta(\xi)$, the Dirac delta function.

χ_r can be defined in several ways,[3] but the one that most naturally generalizes to the quantum mechanical case is

$$\chi_r(\mathbf{p},\mathbf{q}) = \lim_{t\to\infty} h[f(\mathbf{q}(t)] \tag{7}$$

where $\mathbf{q}(t) \equiv \mathbf{q}(t;\mathbf{p},\mathbf{q})$ is the classical trajectory determined by the initial conditions $(\mathbf{p},\mathbf{q})$ at time $t = 0$; thus, $\chi_r\,(\mathbf{p},\mathbf{q}) = 1$ if the trajectory with initial conditions $(\mathbf{p},\mathbf{q})$ is on the product side of the dividing surface as $t \to \infty$, and is 0 otherwise. All of the *dynamics* of the reaction is thus contained in the characterization function χ_r.

It is useful for some purposes to define the *microcanonical* rate constant k(E),

$$k(E) = [2\pi\hbar\rho_r(E)]^{-1}\, N(E) \,, \tag{8}$$

where ρ_r is the density of reactant states (per unit energy), and N(E) is the *cumulative reaction probability*,

$$N(E) = 2\pi\hbar\,(2\pi\hbar)^{-F} \int d\mathbf{p} \int d\mathbf{q}\; \delta[E-H(\mathbf{p},\mathbf{q})]\; F(\mathbf{p},\mathbf{q})\; \chi_r(\mathbf{p},\mathbf{q})\,, \tag{9}$$

where F and χ_r are as above. Since

$$\int_{-\infty}^{\infty} dE\; e^{-\beta E}\; \delta[E-H(\mathbf{p},\mathbf{q})] = e^{-\beta H(\mathbf{p},\mathbf{q})}\,, \tag{10}$$

it is easy to see that the thermal rate k(T), Eq. (1), can be expressed in terms of N(E), Eq. (9), as

$$k(T) = [2\pi\hbar Q_r(T)]^{-1} \int_{-\infty}^{\infty} dE\; e^{-\beta E}\; N(E)\,. \tag{11}$$

For most of this paper, therefore, N(E) will be focused on as the primary object of interest, and the canonical (i.e., thermal) and microcanonical rates are given in terms of it by Eqs. (11) and (8), respectively.

The calculation implied by Eq. (9) for N(E) (or Eq. (1) for k(T)) is therefore to integrate over phase space (**p**,**q**) — in practice usually with Monte Carlo sampling methods — where each phase point (**p**,**q**) serves as the initial conditions for a trajectory that must be run (i.e., numerically integrated) to determine whether χ_r is 1 or 0, i.e., whether or not this phase point contributes to the integral. Because the flux, Eq. (6), contains the factor $\delta[f(\mathbf{q})]$, all trajectories begin on the dividing surface $f(\mathbf{q}) = 0$.

Finally, we note that the rate is independent of the choice of the dividing surface (by virtue of Liouville's theorem) but that a sensible choice for it greatly simplifies the calculation.[6] Referring to Fig. 1, it is intuitively clear that using dividing surface S_1 will require trajectories to be run for a much longer time to determine whether they will wind up on the product side as $t \to \infty$ than if dividing surface S_2 is used.

Transition State Theory

The fundamental assumption of transition state theory is that of *direct* dynamics, i.e., that all trajectories which cross the dividing surface do so only once.[1,3,5] If this is true then a trajectory will be on the product side of the dividing surface at $t \to \infty$ only if it begins at $t = 0$ (on the dividing surface) headed in the product direction, i.e., with positive momentum normal to the dividing surface,

$$\chi_{TST}(\mathbf{p},\mathbf{q}) = h\left[\frac{\partial f(\mathbf{q})}{\partial(\mathbf{q})} \bullet \mathbf{p}/m\right], \tag{12}$$

which may also be thought of as a short time approximation to the dynamics. The resulting phase space integral for N(E) which then follows from Eq. (9) is particularly simple if one chooses a *planar* dividing surface; if q_F is the coordinate normal to the dividing plane, then

$$f(\mathbf{q}) = q_F \tag{13}$$

— i.e., $q_F = 0$ defines the dividing surface — and Eq. (9) then reads

$$N_{TST}(E) = 2\pi\hbar\,(2\pi\hbar)^{-F} \int d\mathbf{q} \int d\mathbf{p}\; \delta[E-V(\mathbf{q})-\frac{\mathbf{p}^2}{2m}]\; \delta(q_F)\frac{p_F}{m}\, h(p_F)\,. \tag{14}$$

The two delta functions in the integrand allow the integrals over q_F and p_F to be carried out, giving

$$N_{TST}(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p}' \int d\mathbf{q}'\; h[E-H^{\ddagger}(\mathbf{p}',\mathbf{q}')]\,, \tag{15}$$

where $(\mathbf{p}',\mathbf{q}') \equiv (p_k,q_k)$, $k = 1, \ldots, F-1$ are the coordinates and momenta for motion *on* the dividing surface defined by $q_F = 0$, and

$$H^{\ddagger}(\mathbf{p}',\mathbf{q}') = \sum_{k=1}^{F-1} \frac{p_k^2}{2m} + V(\mathbf{q}',q_F=0)\,, \tag{16}$$

is the Hamiltonian in this reduced space. In words, Eq. (15) says that the cumulative reaction probability is the volume of phase space of the "activated complex" (the (F-1) dimensional system for motion on the dividing surface) with energy less than or equal to E.

With Eq. (11), the TST expression for the thermal rate then takes its standard form,

$$k_{TST}(T) = \frac{kT}{h} \frac{Q^{\ddagger}(T)}{Q_r(T)} , \tag{17}$$

where $Q^{\ddagger}$ is the partition function of the activated complex,

$$Q^{\ddagger}(T) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p}' \int d\mathbf{q}' \, e^{-\beta H^{\ddagger}(\mathbf{p}',\mathbf{q}')} . \tag{18}$$

An important feature of classical transition state theory is that it is an *upper bound* to the correct result for any choice of the dividing surface. I.e., since all reactive trajectories must cross the dividing surface, but all trajectories that cross it are not necessarily reactive (because they might re-cross it at a later time and be non-reactive), any error in the TST approximation, Eq. (12), is to count some non-reactive trajectories as reactive. Thus, while the exact rate expression does not depend on the choice of the dividing surface, the TST rate does, and by virtue of this bounding property the best choice of the dividing surface is the one which makes k_{TST} a *minimum*. This is the *variational* aspect of TST: any parameters which specify the shape or location of the dividing surface are best chosen to minimize the TST rate.[7]

Transition state theory is often a very good approximation for the classical rate of a chemical reaction. Pechukas *et al.*,[8] in fact, have shown that TST is *exact* at sufficiently low energy. Figs. 2 and 3 show a numerical illustration[9] of this for the standard test reaction $H+H_2 \rightarrow H_2+H$, for the collinear version of the reaction (Fig. 2) and also in three-dimensional space (Fig. 3). In both cases TST is essentially exact up to ~0.3 eV above the potential energy barrier, but for higher energies it begins to be increasingly larger than the correct result. I.e., as the energy increases there is an increasingly larger fraction of trajectories which "rebound" back across the dividing surface and invalidate the transition state assumption that no trajectories re-cross it. One also sees that this fraction of TST-violating trajectories is much smaller in three-dimension space than in one-dimension.

Quantum Transition State Theory

The dynamics of molecular motion must be treated quantum mechanically if one is to have a quantitative description of chemical reactions. Since transition state theory is such a good approximation in classical mechanics — particularly at the lower energies that are most important for determining the thermally averaged rate k(T) — one would like to quantize it. Unfortunately there does not seem to be a way to quantize the basic transition state idea without also introducing other approximations. The heuristic argument goes as follows.

The most naive approach to quantizing the TST expression for N(E), Eq. (15), is as follows: the phase space average becomes a quantum mechanical trace,

$$N^{(0)}_{QMTST}(E) = \mathrm{tr}[h(E-H^{\ddagger})] ,$$

$$= \sum_n h(E-E_n^{\ddagger}) , \tag{19}$$

where $H^{\ddagger}$ is the Hamiltonian operator in the (F-1) dimensional space on the dividing surface, and $\{E_n^{\ddagger}\}$ are the eigenvalues (i.e., energy levels) for this bounded motion. The thermal rate constant which results is easily shown from Eq. (11) to be

$$k^{(0)}_{QMTST}(T) = \frac{kT}{h}\frac{Q^{\ddagger}(T)}{Q_r(T)} , \tag{20}$$

but where here $Q^{\ddagger}(T)$ is the *quantum* partition function

$$Q^{\ddagger}(T) = \sum_n e^{-\beta E_n^{\ddagger}} , \tag{21}$$

which corresponds to the classical one in Eq. (18).

This zeroth order approach, however, neglects any quantum mechanical aspect of the reaction coordinate motion (the Fth degree of freedom). If one assumes that the reaction coordinate is separable for the (F-1) degrees of freedom on the dividing surface, then the

Heaviside function in Eq. (19) is replaced by a one dimensional tunneling probability,

$$N^{(1)}_{QMTST}(E) = \sum_n P_F(E-E_n^{\ddagger}) \ , \tag{22}$$

where $P_F(E_F)$ is the tunneling probability for a one dimensional barrier along the reaction coordinate, as a function of the energy $E_F \equiv E-E_n^{\ddagger}$ in this one degree of freedom. It is easy to show from Eq. (11) that the thermal rate constant corresponding to Eq. (22) is

$$k^{(1)}_{QMTST}(T) = \kappa(T)\,\frac{kT}{h}\,\frac{Q^{\ddagger}(T)}{Q_r(T)} \ , \tag{22$'$}$$

where κ, the tunneling correction factor,

$$\kappa(T) = \beta\int_{-\infty}^{\infty} dE_F\, e^{-\beta E_F}\, P_F(E_F) \ , \tag{21}$$

results as a multiplicative correction.

The reaction coordinate, however, is clearly *not* separable from the (F-1) degrees of freedom on the dividing surface, and at low temperature and for the dynamics of light particles (e.g., hydrogen atoms) the errors resulting from this assumption can be sizeable. A *multidimensional* tunneling correction,[10] one that takes account of coupling between the reaction coordinate and the other degrees of freedom, is thus needed in such cases, and there are a variety of such approximate treatments[11,7] (based primarily on what was learned from semiclassical tunneling calculations[12]). Though many of these are very useful, the only correct multidimensional tunneling correction is to solve the full dimensional Schrödinger equation, but this is then no longer a "theory" but rather simply the exact quantum result. Unlike classical mechanics, therefore, there is no "rigorous" quantum version of TST — i.e., one that does not make some approximations between couplings of the various degrees of freedom — other than the exact quantum dynamical result.

Before proceeding to consider such rigorous quantum treatments, though, it is useful to note that there does exist a "rigorous" semiclassical versions of TST.

Semiclassical Transition State Theory

The starting point[13] for semiclassical TST is to note that the classical Hamiltonian can in general be expressed in terms of a set of locally conserved ("good") action variables associated with the transition state (i.e., saddle point) region of the potential energy surface. The first step in SCTST is thus to determine the classical Hamiltonian $H_{cl}(\mathbf{I}) \equiv H_{cl}(I_1,....,I_F)$ in terms of the F actions $\{I_k\}$. Within a second order perturbative treatment[14] of the anharmonicity, for example, H_{cl} has the form

$$H_{cl}(\mathbf{I}) = V_0 + \sum_{k=1}^{F} \omega_k I_k + \sum_{k \le k'=1}^{F} x_{k,k'} I_k I_{k'} , \tag{23}$$

where $\{\omega_k\}$ are the normal mode frequencies and $\{x_{k,k'}\}$ anharmonic constants that are determined by the cubic and quartic force constants of the potential energy surface. If one were considering vibrational motion about a *minimum* on a potential surface, then these actions would be quantized in the usual semiclassical (Bohr-Sommerfeld) fashion,

$$I_k = (n_k + \frac{1}{2})\hbar , \tag{24}$$

$n_k = 0,1,....$ and Eq. (23) would then yield the vibrational energy levels. For a saddle point H_{cl} has the same form as Eq. (23) (within the perturbative approximation), the only difference being that ω_F, the normal mode frequency associated with the reaction coordinate, is pure imaginary. (Also, of course, one is not thinking of vibrational energy levels in connection with a saddle point, but rather the reaction rate through it.) The (F-1) actions associated with the bounded degrees of freedom are quantized in the usual semiclassical fashion, i.e., via Eq. (24), and the action I_F — the one associated with the reaction coordinate — is pure imaginary and defines the generalized barrier penetration integral θ,

$$\theta \equiv -i\pi I_F/\hbar. \tag{25}$$

θ is determined as a function of total energy E and the (F-1) quantum numbers of the activated complex by energy conservation,

$$H_{cl}[I_k = (n_k+\frac{1}{2})\hbar,\ I_F = i\hbar\theta/\pi] = E\ ; \tag{26}$$

i.e., for $\mathbf{n} \equiv \{n_k\}$, k=1,...,F-1, fixed, one must invert the E-θ relation defined by Eq. (26) to obtain $\theta(E,\mathbf{n})$. Since the dynamics is integrable in terms of the "good" actions, the transmission probability for state **n** and energy E has the same form as in one dimension, i.e., $(1+e^{2\theta})^{-1}$, so the CRP is given by[15]

$$N_{SCTST}(E) = \sum_{\mathbf{n}} \left[1+e^{2\theta(E,\mathbf{n})}\right]^{-1} . \tag{27}$$

The SCTST expression for the thermal rate — which results from Eq. (11) with Eq. (27) for the CRP — can be put in an even more useful form,[16] one that avoids having to invert the E-θ relation in Eq. (26). Thus Eqs. (11) and (27) give the thermal rate as

$$k_{SCTST}(T) = (2\pi\hbar Q_r)^{-1} \sum_{\mathbf{n}} \int_{E_0}^{\infty} dE\, e^{-\beta E}\left(1+e^{2\theta(E,\mathbf{n})}\right)^{-1} , \tag{28}$$

where E_0 is the reaction threshold and where we have interchanged the order of summation and integration. Since one must integrate over all E in Eq. (28), it is equivalent to change the integration variables from E to θ and integrate over all θ,

$$\begin{aligned}\int_{E_0}^{\infty} dE\, e^{-\beta E}\left(1+e^{2\theta(\mathbf{n},E)}\right)^{-1} &= \int_{\infty}^{-\infty} d\theta\, \frac{\partial E(\mathbf{n},\theta)}{\partial\theta}\, e^{-\beta E(\mathbf{n},\theta)}\left(1+e^{2\theta}\right)^{-1} \\ &= \frac{1}{\beta}\int_{-\infty}^{\infty} d\theta\, e^{-\beta E(\mathbf{n},\theta)}\, \frac{1}{2}\mathrm{sech}^2(\theta) ,\end{aligned} \tag{29}$$

where the last line results from an integration by parts. (The surface terms vanish because $E(\theta\to\infty) = E_0$, the reaction threshold, and $E(\theta\to-\infty) = \infty$.) Use of Eq. (29) in Eq. (28) then gives

$$k_{SCTST}(T) = (2\pi\hbar Q_r\beta)^{-1} \int_{-\infty}^{\infty} d\theta\, \frac{1}{2}\mathrm{sech}^2(\theta) \sum_{\mathbf{n}^{\ddagger}} e^{-\beta E(\mathbf{n}^{\ddagger},\theta)} , \tag{30}$$

where we have again changed the order of summation and integration. Noting that $(2\pi\hbar\beta)^{-1} = kT/h$, Eq. (30) takes the form of the traditional TST,

$$k_{SCSTS}(T) = \frac{kT}{h}\frac{Q^{\ddagger}(T)}{Q_r(T)} , \tag{31a}$$

by defining the reactive partition function of the activated complex (including the tunneling correction factor which is not separable from it) as an average of the fixed θ partition function $Q^{\ddagger}(T,\theta)$ with the weight function $\frac{1}{2}\mathrm{sech}^2(\theta)$,

$$Q^{\ddagger}(T) = \int_{-\infty}^{\infty} d\theta \frac{1}{2}\mathrm{sech}^2(\theta) Q^{\ddagger}(T,\theta) \ . \tag{31b}$$

where

$$Q^{\ddagger}(T,\theta) \equiv \sum_{\mathbf{n}} e^{-\beta E(\mathbf{n},\theta)} \ . \tag{31c}$$

Applications[16] have demonstrated the usefulness of this formulation of the k(T) calculation.

These SCTST expressions, in both the microcanonical [Eq. (27)] and canonical [Eq. (31)] forms, include coupling between all the degrees of freedom in a uniform manner. E.g., even at the perturbative level, Eq. (23), there is anharmonic coupling between modes of the activated complex ($x_{k,k'}$, k and $k' \leq F-1$) and between the reaction coordinate and modes of the activated complex ($x_{k,F}$, $k \leq F-1$). This is not a dynamically exact theory, however, because these actions variables are in general only locally "good". For energies too far above or below the barrier V_0 they may fail to exist. This semiclassical theory is thus still a transition state "theory" (i.e., dynamical approximation).

Rigorous Quantum Rate Theory

The completely rigorous equilibrium rate constant can also be written in the form of Eq. (11), where for a bimolecular reaction the rigorous expression for the cumulative reaction probability is[17]

$$N(E) = \sum_{n_p} \sum_{n_r} |S_{n_p,n_r}(E)|^2 \ , \tag{32}$$

where $n_r(n_p)$ denote all the quantum numbers of the reactants (products), and the square moduli of the S-matrix elements are the reaction probabilities for the $n_r \rightarrow n_p$ (state-to-state) transition. It is Eq. (32), in fact, which suggests the term "cumulative reaction probability" for N(E): i.e., the *total* reaction probability from initial reactant state n_r is given by

$$P_{n_r}(E) \equiv \sum_{n_p} |S_{n_p,n_r}(E)|^2 , \tag{33a}$$

and if one idealized matters by assuming that some initial states are completely reactive and others completely non-reactive, i.e., $P_{n_r} = 0$ or 1, then clearly N(E),

$$N(E) \equiv \sum_{n_r} P_{n_r}(E) . \tag{33b}$$

would be the number of reactive states. This interpretation as the "number of reactive states" also comes from transition state theory, cf. Eq. (19), where there N is the number of states of the activated complex that lie below total energy E, i.e., which have positive kinetic energy in the reaction coordinate at the transition state. In reality, of course, reaction probabilities can take on any values between 0 and 1, but the interpretation of N(E) as the effective number of quantum states which react is still qualitatively useful.

Though Eq. (32) provides a rigorous quantum definition of the cumulative reaction probability, is not helpful in a practical sense because a complete state-to-state reactive scattering calculation is required to obtain the S-matrix. We seek a more direct (and thus presumably more efficient) route to N(E), but without approximation, to which approximations can be incorporated later as needed in specific applications.

A formally exact (and 'direct') expression for N(E) can be obtained by quantizing the dynamically exact classical expression, Eq. (9) [with Eq. (7)]; the classical phase space average becomes a quantum trace, and classical functions become operators:

$$N(E) = 2\pi\hbar \, \mathrm{tr}[\delta(E-\hat{H}) \, \hat{F} \, \hat{\chi}_r] , \tag{34}$$

where

$$\hat{\chi}_r = \lim_{t\to\infty} h[f(\hat{\mathbf{q}}(t))] ,$$

and we note that quantum mechanical time evolution is expressed as

$$\hat{\chi}_r = \lim_{t\to\infty} e^{i\hat{H}t/\hbar} \, h[f(\mathbf{q})] \, e^{-i\hat{H}t/\hbar} . \tag{35}$$

($\hat{\chi}_r$ is a projection operator that projects onto all state that are on the product side of the dividing surface in the infinite future.) The long time limit can also be written as the integral of the time derivative,

$$\lim_{t\to\infty} h[f(\hat{\mathbf{q}}(t))] = \int_0^\infty dt \frac{d}{dt} h[f(\hat{\mathbf{q}}(t))]$$

$$= \int_0^\infty dt\ e^{i\hat{H}t/\hbar}\ \hat{F}\ e^{-i\hat{H}t/\hbar}\ , \tag{36}$$

where $\hat{F}$ is the flux operator,

$$\hat{F} = \frac{i}{\hbar}\ [\hat{H}, h(\hat{f}(\mathbf{q}))]\ . \tag{37}$$

Interchanging the order of the trace and the time integral, and noting that the (real part of the) integrand is even, then gives

$$N(E) = (2\pi\hbar)\frac{1}{2}\int_{-\infty}^{\infty} dt\ \mathrm{tr}\ [\delta(E-\hat{H})\hat{F}e^{i\hat{H}t/\hbar}\ \hat{F}e^{-i\hat{H}t/\hbar}]\ .$$

But the operator $e^{-i\hat{H}t/\hbar}$ can be replaced by the scalar $e^{-iEt/\hbar}$ since this operator sits next to $\delta(E-\hat{H})$ (with a cyclic permutation inside the trace), and with the identity

$$\int_{-\infty}^{\infty} dt\ e^{i(H-E)t/\hbar} = 2\pi\hbar\delta(E-\hat{H})\ ,$$

one obtains the following result[18]

$$N(E) = \frac{1}{2}\ (2\pi\hbar)^2\ \mathrm{tr}(\hat{F}\delta(E-\hat{H})\ \hat{F}\delta(E-\hat{H})]\ . \tag{38}$$

Equation (38) is quite a beguiling expression. E.g., in the classical expression for N(E), Eq. (9), there is a *statistical* factor $\delta(E-H)$, the flux factor F, and a *dynamical* factor χ. A similar structure exist in the quantum expression, Eq. (34), where the dynamical factor is the projection operator $\hat{\chi}_r$. The manipulations following Eq. (35), however, lead to the result, Eq. (38), which appears to have *no* dynamical information; i.e., only the statistical operator $\delta(E-\hat{H})$ and flux operator $\hat{F}$ are involved in Eq. (38). This is an example of the fact that dynamics and statistics are inseparably intertwined in quantum mechanics; e.g., a wavefunction describes the *dynamical motion* of the particles and also their *statistics*. Finally, note that one cannot convert Eq. (38) directly into a corresponding classical expression by replacing the trace by a phase space average and the

operators by the corresponding functions (as one *can* do for Eq. (34)). If one tries, the result is

$$N(E) = \frac{1}{2}\,(2\pi\hbar)^2\,(2\pi\hbar)^{-F}\int d\mathbf{p}\int d\mathbf{q}\;\delta(E-H(\mathbf{p},\mathbf{q}))^2\;F(\mathbf{p},\mathbf{q})^2\,, \tag{39}$$

which appears to be infinite (because of the squares of the delta functions); the factor $\hbar^2$ (which doesn't divide out in normalization) is 0 in the classical limit, however, so Eq. (39) is simply indeterminant.

The difficult part of Eq. (38) to evaluate is the microcanonical density operator, $\delta(E-\widehat{H})$, which is usually[19] expressed in terms of the outgoing wave Green's function (actually an *operator*),

$$\delta(E-\widehat{H}) = -\frac{1}{\pi}\,\mathrm{Im}\,\widehat{G}^{+}(E)\,, \tag{40a}$$

where

$$\widehat{G}^{+}(E) = \lim_{\varepsilon\to 0}\;(E+i\varepsilon-\widehat{H})^{-1}\,. \tag{40b}$$

ε is a positive constant which imposes the outgoing wave boundary condition on the Green's function (hence the "+" designation), or it may be thought of as a convergence factor in the expression for G^+ in terms of the time evolution operator $e^{-i\widehat{H}t/\hbar}$

$$\widehat{G}^{+}(E) = (i\hbar)^{-1}\int_0^{\infty} dt\; e^{i(E+i\varepsilon)t/\hbar}e^{-i\widehat{H}t/\hbar}\;;$$

the factor $\exp(-\varepsilon t/\hbar)$ in the integrand makes the time integral well-behaved in the long time ($t\to\infty$) limit.

The parameter ε in Eq. (40b) usually plays a purely formal role in quantum scattering theory, but it has recently[4a] been pointed out that one may think of it as the *absorbing potential* that a number of persons[20] have used in numerical wavepacket propagation calculations to prevent reflections at the edge of the coordinate space grid. In this latter approach one adds a negative imaginary potential to the true potential energy function,

$$V(\mathbf{q}) \to V(\mathbf{q}) - i\varepsilon(\mathbf{q})\,, \tag{41a}$$

but this is clearly equivalent to adding the positive (operator) ε to E in E-H,

$$E-\hat{H} \rightarrow E + i\hat{\varepsilon}(q) - \hat{H} . \tag{41b}$$

Allowing ε to be a (positive) function of coordinates, i.e., a potential energy operator, is better than taking it to be a constant, because it can be chosen to be zero in the physically relevant region of space and only "turned on" at the edges of this region to impose the outgoing wave boundary condition. Absorbing flux in this manner, and thus not allowing it to return to the interaction region, is analogous in a classical calculation to terminating trajectories when they exit the interaction region.

Figure 4 shows a sketch of the potential energy surface for the generic reaction $H+H_2 \rightarrow H_2+H$, with the absorbing potential $\varepsilon(\mathbf{q})$ indicated by dashed contours. $\varepsilon(\mathbf{q})$ is zero in the transition state region, where the reaction dynamics (i.e., tunneling, re-crossing dynamics, etc.) takes place, and is turned on outside this region. In practice one chooses the interaction region (that between the absorbing potentials) to be as small as possible, so that as small a basis set as possible can be used to represent the operators and evaluate the trace. Choosing it too small, though, will cause the absorbing potentials to interfere with reaction dynamics one is attempting to describe.

With the microcanonical density operator given by Eq. (40) (with some choice for ε), straightforward algebraic manipulations (also using Eq. (37)) lead to the following even simpler form for the cumulative reaction probability,[4b]

$$N(E) = 4 \text{ tr } [\hat{G}^{+}(E)^{*} \hat{\varepsilon}_p \hat{G}^{+}(E)\hat{\varepsilon}_r] , \tag{42a}$$

where $\varepsilon_r(\varepsilon_p)$ is the part of the adsorbing potential in the reactant (product) valley, and $\varepsilon \equiv \varepsilon_r + \varepsilon_p$. This expression may be evaluated in any convenient basis set which spans the interaction region and also extends some ways into the absorbing region. The explicit matrix expression is then

$$N(E) = 4 \text{ tr } [(E-i\varepsilon-\mathbf{H})^{-1} \bullet \varepsilon_p \bullet (E+i\varepsilon-\mathbf{H})^{-1} \bullet \varepsilon_r] , \tag{42b}$$

with

$$\varepsilon = \varepsilon_r + \varepsilon_p .$$

It is interesting to note that in Eq. (42) all reference to a specific dividing surface has vanished; it is implicit that a dividing surface lies somewhere between the reactant and product "absorbing strips" (cf. Fig. 4), but there is no dependence on its specific choice. This is consistent with the earlier discussion that in classical mechanics N(E) is independent of the choice of the dividing surface provided that one actually determines the exact dynamics, as is being done here quantum mechanically.

Eq. (42) provides the first practical scheme for determining the rate constant for a chemical reaction absolutely *correctly*, but *directly*, i.e., without having to solve the complete reactive scattering problem. This is not a transition state "theory" since calculation of the Green's function, the matrix inverse of $(E+i\varepsilon-\mathbf{H})$, is equivalent to solving the Schrödinger equation, i.e., it generates the complete quantum dynamics. Since this is required only in the transition state region (between the reactant and product absorbing strips), one may think of this quantum mechanical calculation as the analog of a classical trajectory calculation which begins trajectories on a dividing surface in the transition state region and follows them for a short time to see which ones are reactive.

Illustrative Examples

In recent applications[4] it has proved useful to employ a set of *grid points* in coordinate space as the basis set in which to evaluate Eq. (42b). These discrete variable,[21] pseudo-spectral,[22] or collocation methods[23] are proving quite useful for a variety of molecular quantum mechanical calculations. The primary advantages of such approaches are that (1) no integrals are required in order to construct the Hamiltonian matrix (e.g., the potential energy matrix is diagonal, the diagonal values being the values of the potential energy function at the grid points), and (2) the Hamiltonian matrix is extremely sparse (so that large systems of linear equations can be solved efficiently).

Since the absorbing potential is diagonal in a grid point representation, Eq. (42b) for the cumulative reaction probability simplifies to

$$N(E) = 4 \sum_{i,i'} \varepsilon_i^r |G_{i,i'}|^2 \varepsilon_{i'}^p , \tag{43}$$

where the index labels the grid points (the "basis functions") and $G_{i,i'}$ is the (i,i′) element of the inverse of the matrix $\{\delta_{i,i'} (E+i\varepsilon_i)-H_{i,i'}\}$, with $\varepsilon_i = \varepsilon_i^r + \varepsilon_i^p$. The sum over i and i′ includes only points in the reactant and product absorbing regions, respectively, since ε_i^r and $\varepsilon_{i'}^p$ are zero at other grid points.

Figure 4c shows the set of grid points and the absorbing potentials which yield accurate results for the standard test problem, the collinear $H+H_2 \rightarrow H_2+H$ reaction. The important feature to see here is how to close the absorbing potentials can be brought in and how localized the grid can be taken about the transition state region. This is the region in which it is necessary to determine the quantum dynamics in order to obtain the correct result for N(E) (and thus k(T)). No information about reactant and product quantum states is involved in the calculation.

Figure 5a shows the cumulative reaction probability so obtained[4a] for the collinear $H+H_2$ reaction. Apart from noting that it is correct (by comparison with any number of earlier scattering calculations using Eq. (32)), it is interesting to observe that at the higher energies N(E) is not a monotonically increasing function of energy. This is a signature[24] of transition state theory-violating dynamics, i.e., re-crossing trajectories in a classical picture, and the result of a short-lived collision complex that causes resonances in a quantum description.

For the $H+H_2$ reaction in three dimensional space one needs to add in the bending degree of freedom in the transition state region and also allow the three-atom system to rotate. Fig. 5b shows the cumulative reaction probability obtained[4b] for zero total angular momentum (J=0), and again it is in complete agreement with results[25] obtained from Eq. (32) via full scattering calculations. Even though collision complexes also form in the

three-dimensional version of the $H+H_2$ reaction, N(E) in Fig. 5b appears (to the eye, at least) to increase monotonically with energy in transition state-like fashion. This is the quantum mechanical analog of the phenomenon seen above classically,[9] where the dynamics behaves more transition state-like the higher the physical dimension of the system.

A more challenging application[26] is to the reaction

$$H+O_2 \rightarrow OH+O\ ,$$

which is one of the most important reactions for modeling the combustion of hydrocarbons. Fig. 6 shows a schematic of the potential surface, and one sees why this is a more complicated reaction to deal with: the deep well (~2 eV) in the interaction region leads to the formation of a moderately long-lived collision complex, strongly violating the transition state assumption of "direct dynamics". The rigorous quantum methodology described above, however, is nevertheless applicable: absorbing potentials are introduced just outside the interaction region where all the reaction dynamics (tunneling, re-crossings, etc.) is determined, and the grid points cover the region in between. Figure 7 shows the cumulative reaction probability for this reaction (for J=0 total angular momentum), and structure resulting from the collision complex is readily observable.

Finally, at the time of this writing, full (six-) dimensional calculations for the CRP of the reaction[27]

$$H+H_2O \rightarrow H_2+OH$$

are being completed, and the reference to this work will be supplied at proof stage.

Cumulative Reaction Probability as an Eigenvalue Problem

To conclude I describe some recent developments[28] that facilitate the evaluation of Eq. (42). Since the absorbing potentials are positive operators (and diagonal in a grid point

representation), it is easy to symmetrize the operand of the trace in Eq. (42),

$$N(E) = \mathrm{tr}[\widehat{P}(E)] \ , \tag{44a}$$

where

$$\widehat{P}(E) \equiv 4\widehat{\varepsilon}_r^{\,1/2}\widehat{G}(E)^*\widehat{\varepsilon}_p\widehat{G}(E)\widehat{\varepsilon}_r^{\,1/2} \ . \tag{44b}$$

$\widehat{P}(E)$ is seen to be a Hermitian operator (or matrix), so that its eigenvalues $\{p_k(E)\}$ are are all real, and from Eq. (44a) the CRP is their sum,

$$N(E) = \sum_k p_k(E) \ . \tag{45}$$

It is also easy to see that $\widehat{P}(E)$ is a positive operator (since it has the form $L^{\dagger}L$), so that its eigenvalues are all positive. It is not as obvious — but can be readily shown — that $\widehat{P}(E)$ is also bounded by the identity operator

$$\widehat{P}(E) \le 1 \ , \tag{46a}$$

from which it follows that

$$0 \le p_k(E) \le 1 \ , \tag{46b}$$

The eigenvalues $\{p_k\}$ can thus be thought of as *probabilities*, and then Eq. (45) bears an interesting relation to the simple transition state expression, Eq. (22), in which N(E) is given (approximately) as a sum of one-dimensional tunneling (or transmission) probabilities over all states of the activated complex. The *exact* N(E) is given in Eq. (45) as the sum of the "eigen reaction probabilities" $\{pk\}$, the eigenvalues of the operator $\widehat{P}$ defined by Eq. (44b).

Finally, since one only needs the eigenvalues of $\widehat{P}$, one can do equally well with the eigenvalues of $\widehat{P}(E)^{-1}$,

$$\widehat{P}(E)^{-1} = \frac{1}{4}\widehat{\varepsilon}_r^{\,-1/2}(E+i\widehat{\varepsilon}-\widehat{H})\widehat{\varepsilon}_p^{\,-1}(E-i\widehat{\varepsilon}-\widehat{H})\widehat{\varepsilon}_r^{\,-1/2} \ . \tag{47}$$

The eigenvalues of $\widehat{P}^{-1}$ are $\{\frac{1}{p_k}\}$, the reciprocals of the desired values. The advantage of working with $\widehat{P}^{-1}$ is clear — it is not necessary to obtain the Greeen's function in order to construct this matrix; it is readily available from the Hamiltonian itself. The most powerful

and efficient approach currently available, therefore, is to determine the eigenvalues of the matrix $\widehat{P}^{-1}$ defined in Eq. (47), the reciprocals of which are the desired eigen reaction probabilities $\{p_k\}$. The reader is referred to the original literature[28] for more specifics of this approach to the calculation.

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to the incident flux (or flux per unit area for the three-dimensional case). These ratios have the more physically meaningful interpretation of an average reaction probability in the collinear case (Figure 2) and an average reaction cross section in the three-dimensional case (Figure 3).

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24. N(E) will always increase monotonically with E in a transition state approximation. It is easy to prove this classically, e.g., from Eq. (15). If the dividing surface is held fixed as E varies, then from Eq. (15) one has

$$\frac{d}{dE} N_{TST}(E) = (2\pi\hbar)^{-(F-1)} \int d\mathbf{p}' \int d\mathbf{q}' \, \delta[E-H^{\ddagger}] ,$$

which is clearly positive. Furthermore, if the dividing surface is parameterized and allowed to vary with energy, the above equation still holds because any parameters in the dividing surface are chosen variationally. Thus if the dividing surface (and thus the Hamiltonian $H^{\ddagger}$) depend on some parameters $c_1, c_2, \ldots = \{c_k\}$, then the expression for N_{TST} will depend not only on the energy E but also on these parameters, $N_{TST}(E, c_1, c_2, \ldots)$. The values of the c_k's are chosen, however, by the variational condition

$$0 = \frac{\partial}{\partial c_k} N_{TST}(E, \{c_k\}) ,$$

which determines specific values $c_k(E)$. Thus the variationally optimized result for the cumulative reaction probability is $N_{TST}(E, c_1(E), c_2(E), \ldots) \equiv N_{TST}(E)$. Then

$$\frac{d}{dE} N_{TST}(E) = \frac{\partial}{\partial E} N_{TST}(E\{c_k\}) + \sum_k \frac{\partial N_{TST}}{\partial c_k} \dot{c}_k(E) ,$$

but the last terms are all zero because of the variational conditions.

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Figure Captions

1. (a) Schematic depiction of the contours of a potential energy surface with two possible choices of the dividing surface (actually a *line* in this two dimensional case), S_1 in the reactant region and S_2 through the transition state region.

   (b) Same as (a), but indicating a region of some width about the dividing surface S_2.

2. Reaction probability for the collinear $H+H_2$ reaction on the Porter-Karplus potential surface from a microcanonical classical trajectory calculation (CLDYN) and microcanonical classical transition-state theory (CLTST), as a function of total energy above the barrier height (1 eV = 23.06 kcal/mole).

3. Same as Figure 1, except that $\sigma(E)$ is the microcanonical reactive cross section for the three-dimensional $H+H_2$ reaction.

4. Solid lines are contours of the potential energy surface for the $H+H_2 \rightarrow H_2+H$ reaction. Broken lines are contours of the absorbing potential (which is zero in the central part of the interaction region and "turned on" at the edge), for three possible choices of it. The points are the grid points which constitute the "basis set" for the evaluation of the quantum trace, Eq. (42).

5. Cumulative reaction probability for the $H+H_2 \rightarrow H_2+H$ reaction, (a) for collinear geometry (ref. 4a), (b) three dimensional space for total angular momentum J=0 (ref. 4b).

6. Energetics (in eV) of the H-O-O potential energy surface.

7. The cumulative reaction probability, for the $H+O_2 \rightarrow OH+O$ reaction as a function of total energy, for total angular momentum J=0.

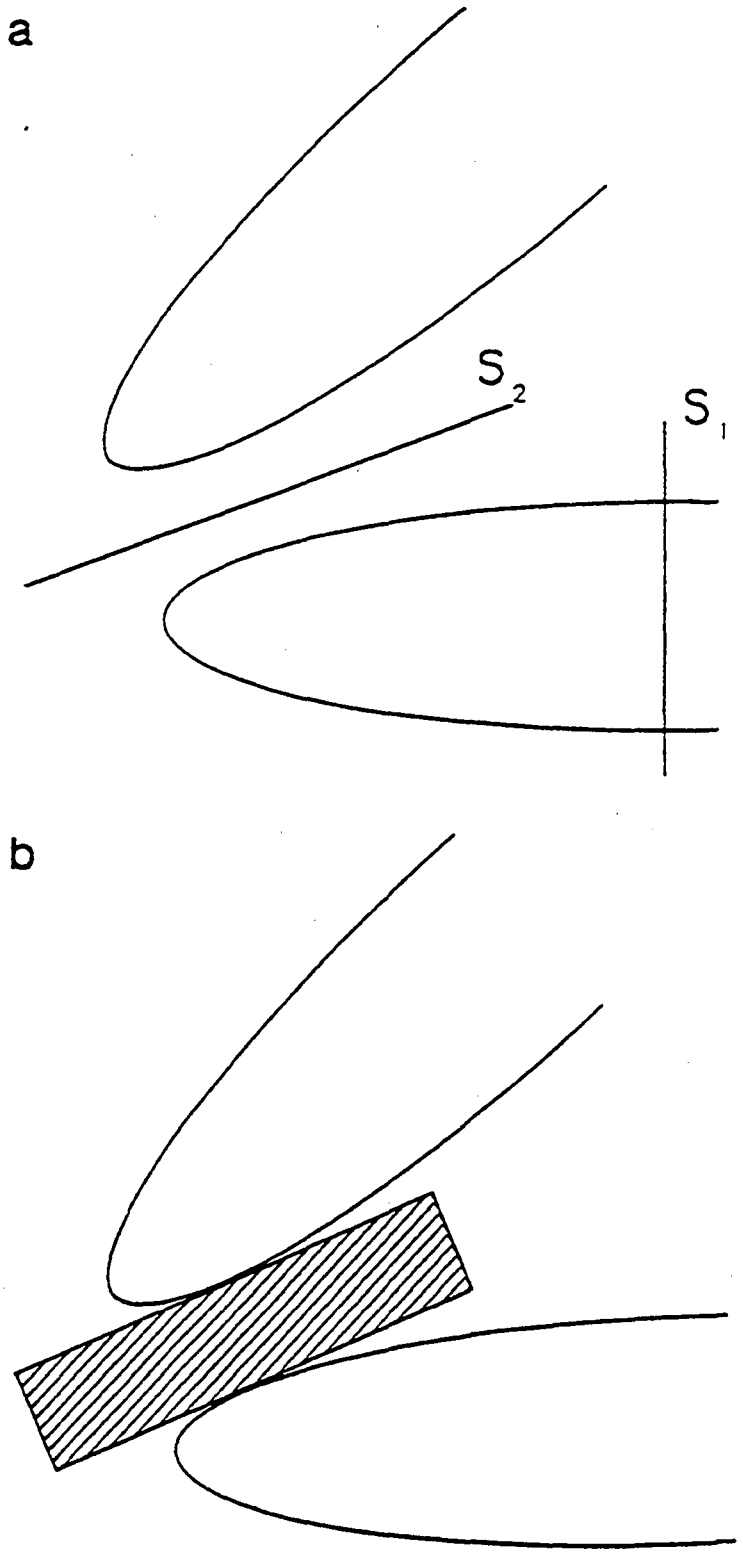

Figure 1

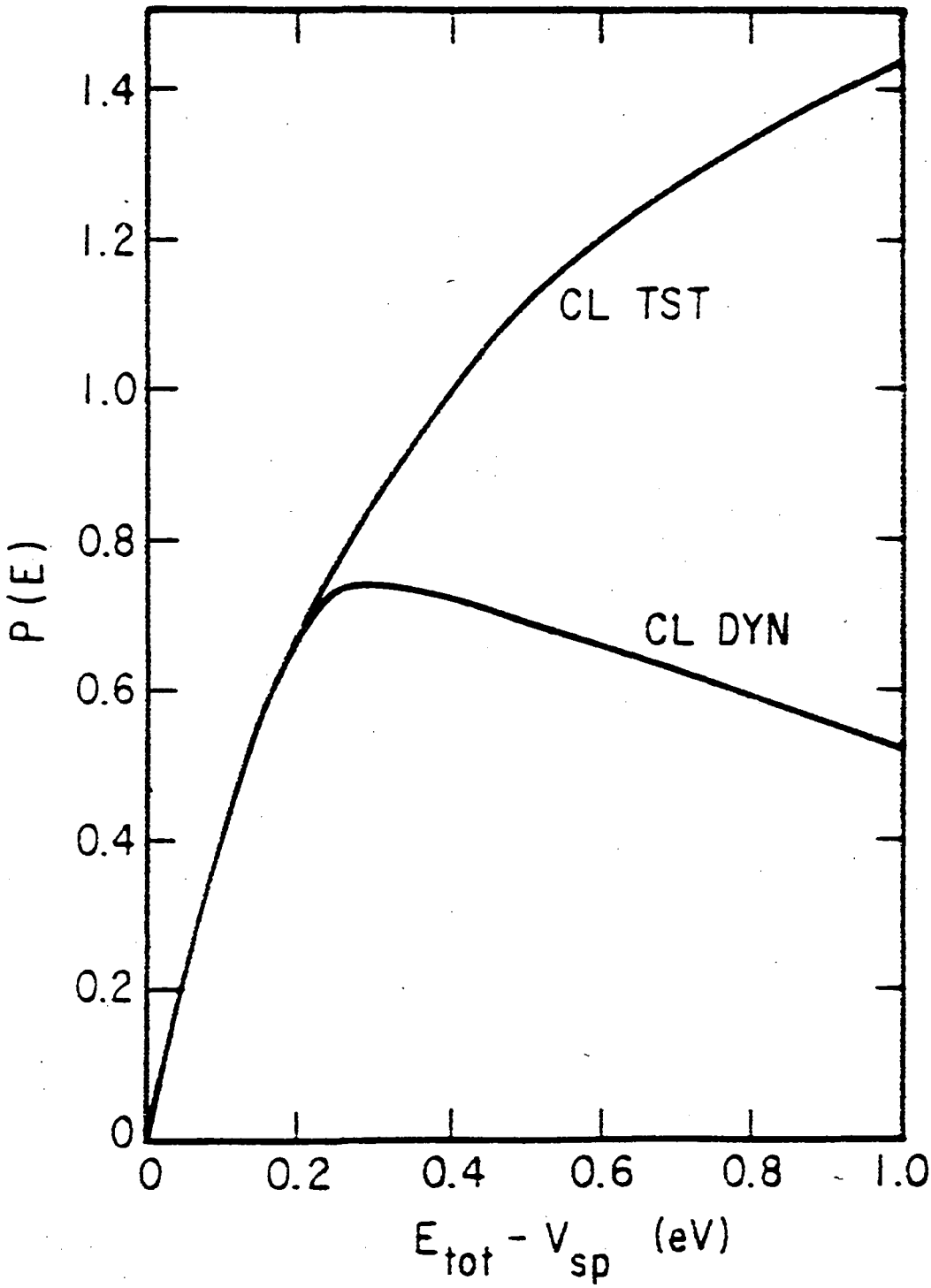

Figure 2

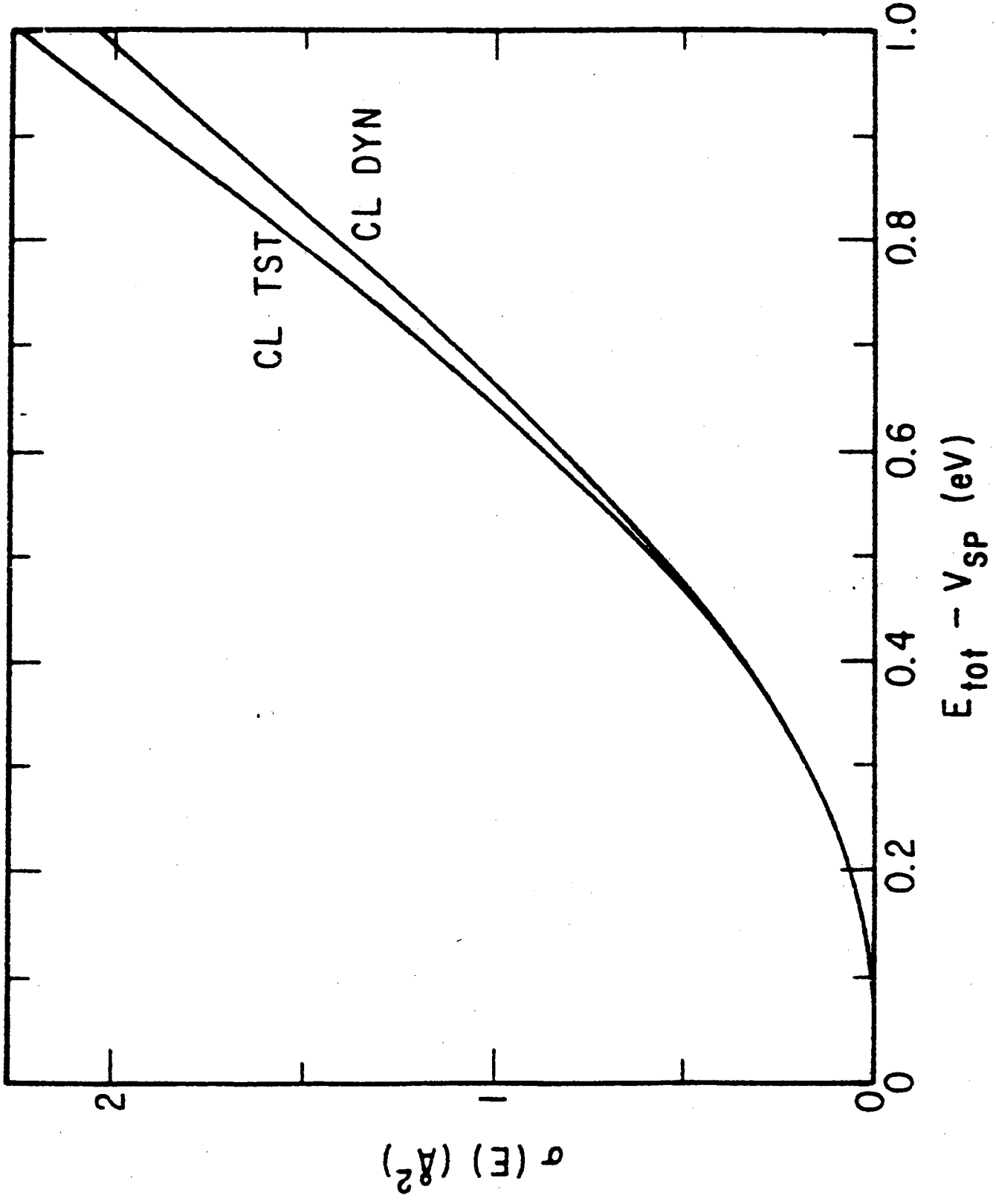

Figure 3

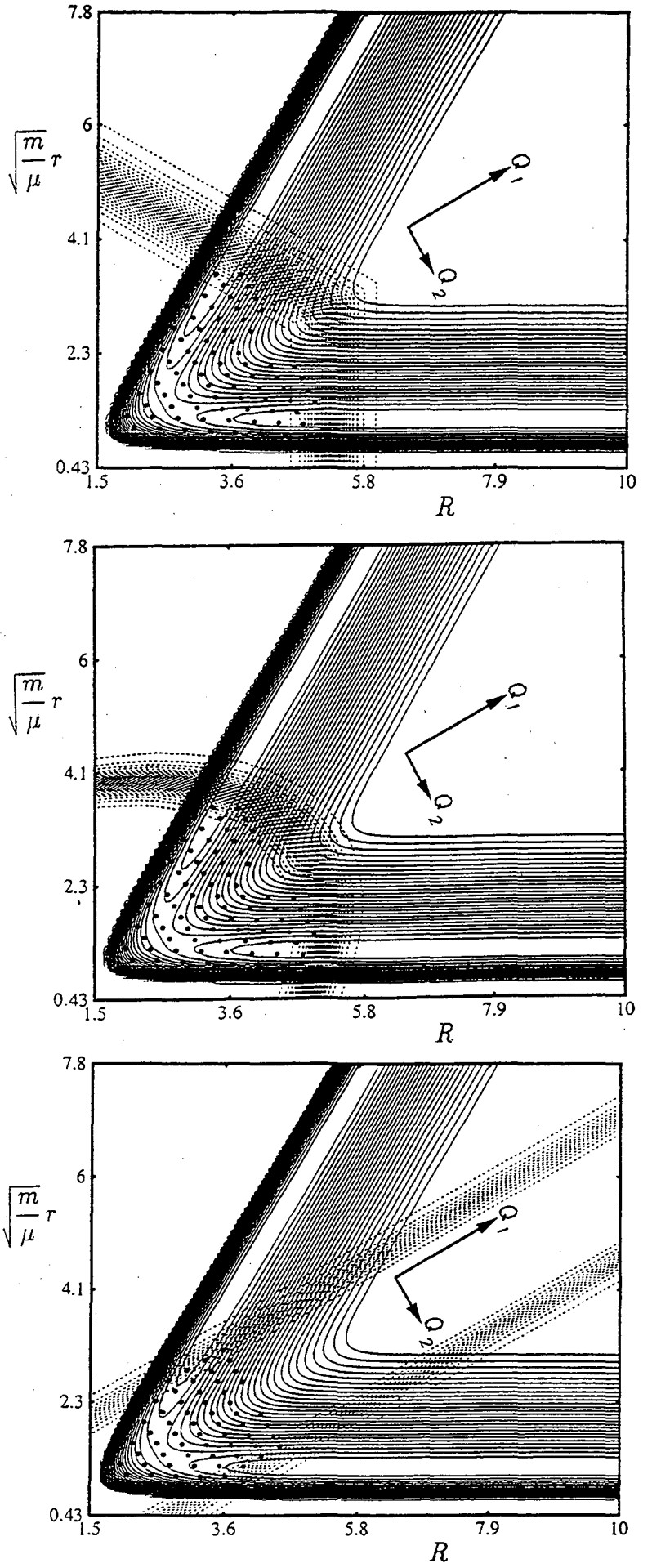

Figure 4

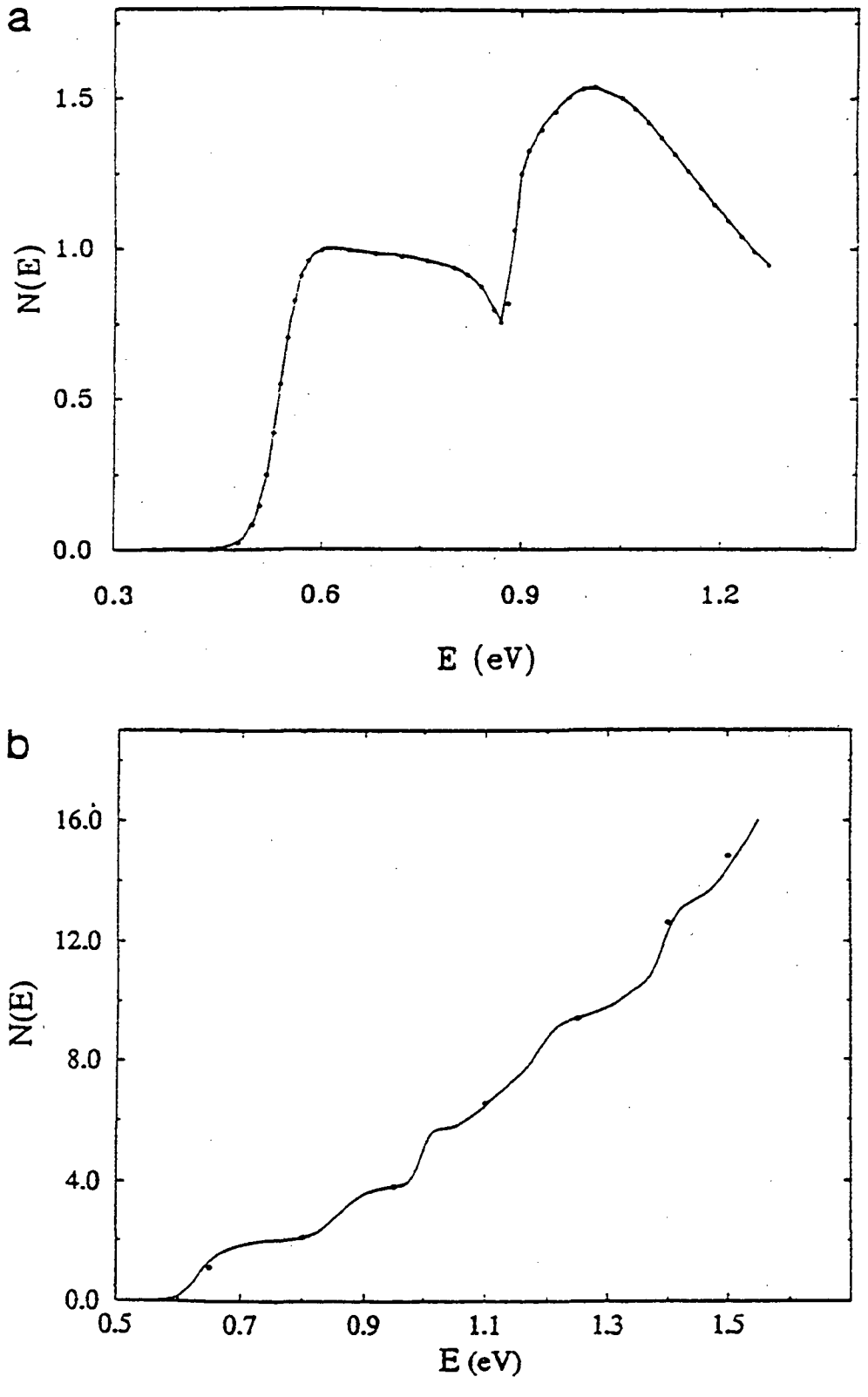
a
1.5
1.0
0.5
0.0
N(E)
0.3
0.6
0.9
1.2
E (eV)
b
16.0
12.0
8.0
4.0
0.0
N(E)
0.5
0.7
0.9
1.1
1.3
1.5
E (eV)

Figure 5

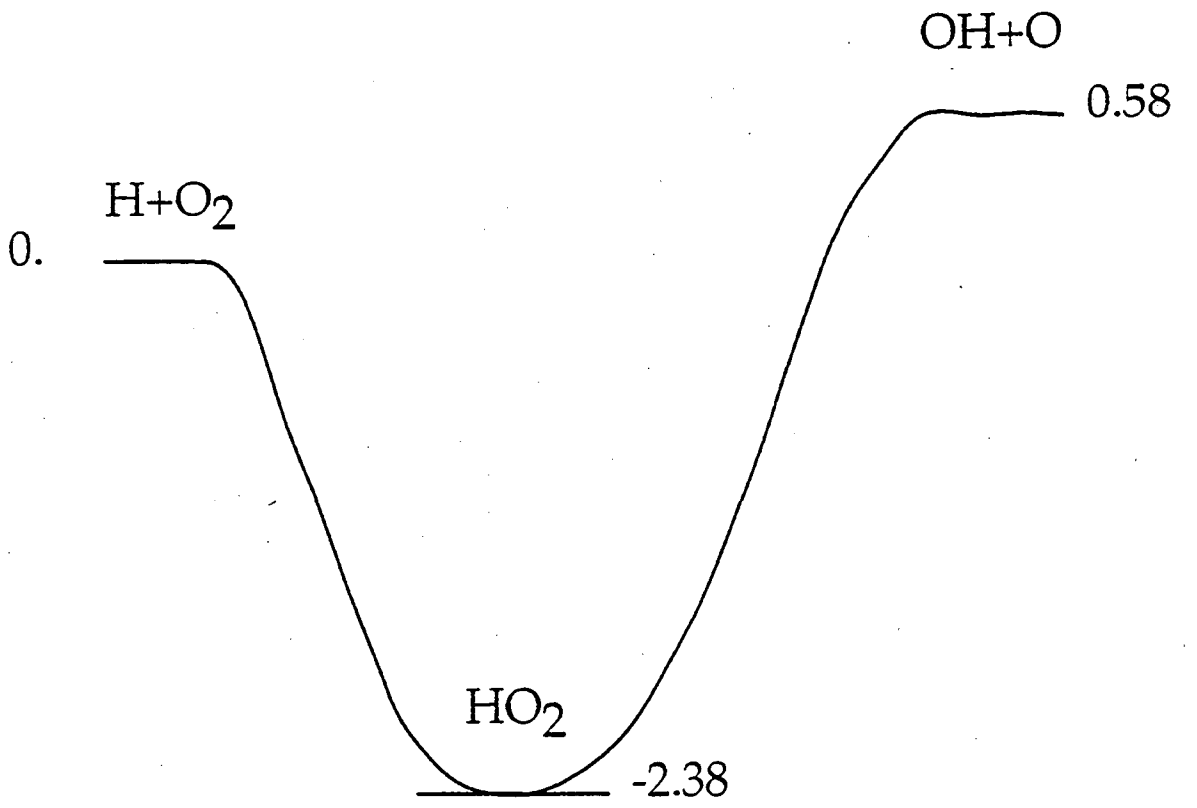

Figure 6

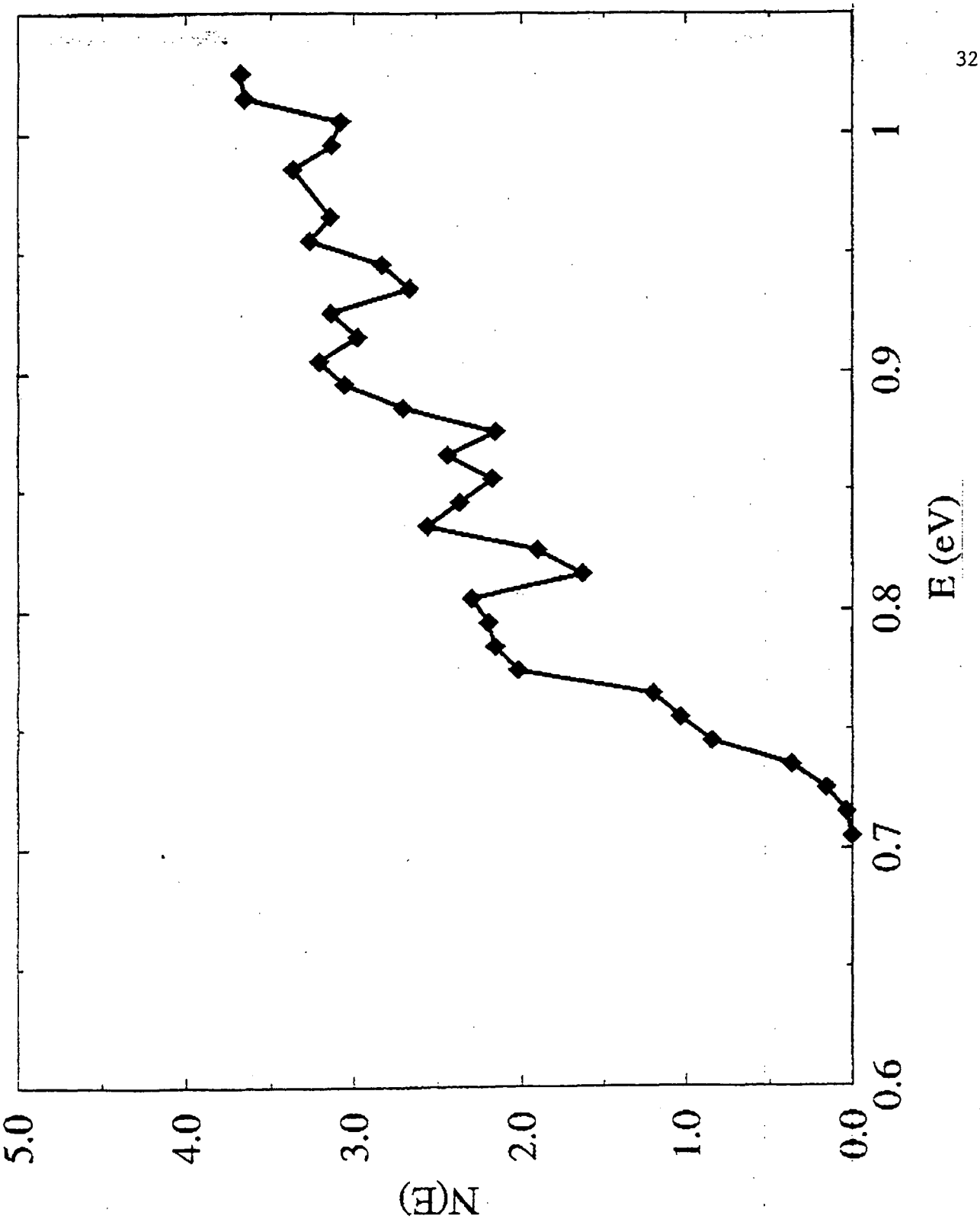

Figure 7

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