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Author

Lester, W.A.

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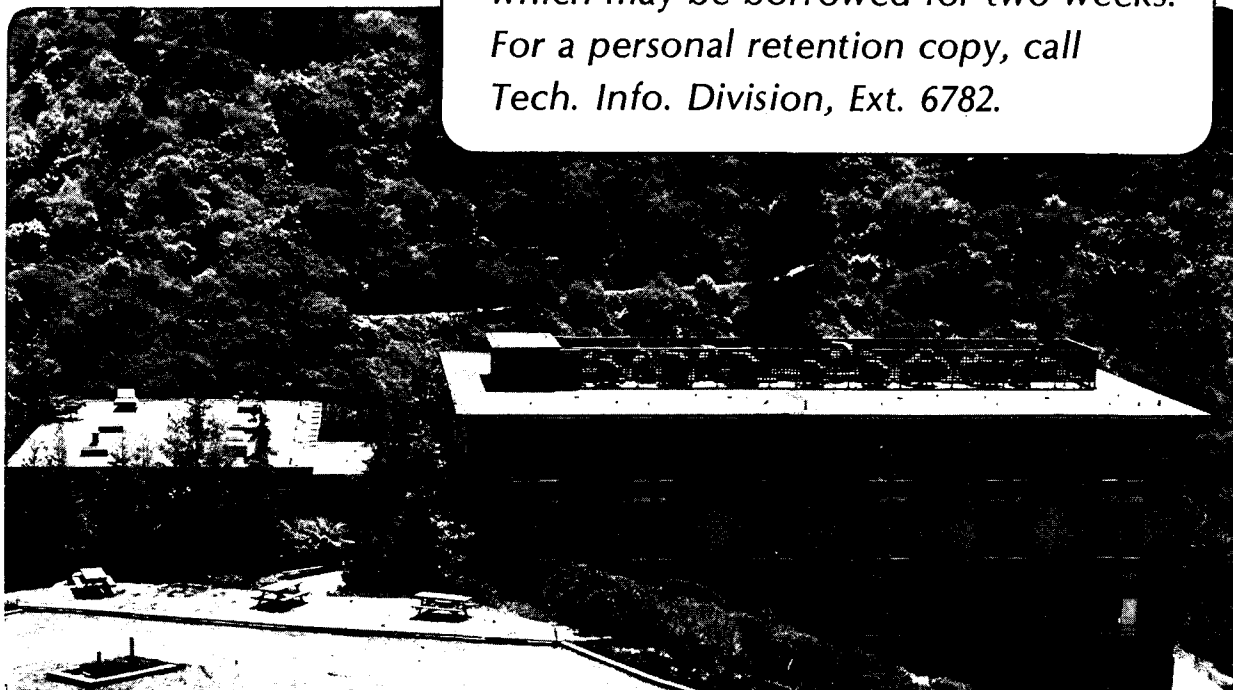
QUANTUM MONTE CARLO STUDY OF THE CLASSICAL BARRIER
HEIGHT FOR THE $H + H_2$ EXCHANGE REACTION: RESTRICTED
VERSUS UNRESTRICTED TRIAL FUNCTIONS

P.J. Reynolds, R.N. Barnett, and W.A. Lester, Jr.

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QUANTUM MONTE CARLO STUDY OF THE CLASSICAL BARRIER HEIGHT FOR THE
H + H₂ EXCHANGE REACTION:
RESTRICTED VERSUS UNRESTRICTED TRIAL FUNCTIONS

P. J. Reynolds,* R. N. Barnett,+ W. A. Lester, Jr.+
Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

The fixed-node quantum Monte Carlo (QMC) method is used to obtain the classical barrier height for the H + H₂ exchange reaction. Using a spin-restricted, single determinant trial function Ψ_T , we find that the reaction barrier E_b is less than 9.69 ± 0.25 kcal/mole. This mean value is below the calculated energy barrier obtained by Liu in the most extensive CI calculations on this system. Furthermore, the QMC saddle point energy of -1.65903 ± 0.00040 hartrees at the CI-determined geometry lies 0.00027 a.u. (0.17 kcal/mole) below Liu's best CI value. Finally, spin-restricted and spin-unrestricted single determinant trial functions are contrasted. Although the variational energy $\langle \Psi_T | H | \Psi_T \rangle$ for an SCF Ψ_T must be lower for the unrestricted case, this is not true generally

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for QMC. In fact, we show that if the unrestricted SCF Ψ_T has the lower QMC energy, then there exists another spin-restricted, single-determinant Ψ_T whose QMC energy is lower than the QMC energy of the spin-restricted SCF Ψ_T .

I. Introduction

The hydrogen exchange reaction $H + H_2 \rightarrow H_2 + H$ is perhaps the simplest of chemical reactions. As such it has been the testing ground for theories of chemical kinetics and collision dynamics [1]. An accurate potential energy surface is needed at the base of these theories. Thus, many studies of the H_3 energy surface, both semi-empirical and ab initio, have been performed [2-4]. Experimental work on the $H + H_2$ reaction [5] provides rate constants, cross sections, and other information describing the collision dynamics, but does not give a direct quantitative description of the H_3 energy surface. Instead, the configuration interaction (CI) method has provided the results that serve as the standard of comparison. By this method accuracy of better than 1 kcal/mole has been obtained [3]. Quite recently, Liu has extended these calculations at the H_3 saddle point, achieving an accuracy on the order of 0.1 kcal/mole [4]. His motivation, at least in part, was to provide a calibration for the quantum Monte Carlo (QMC) random walk method [6].

Here we use the QMC approach to calculate the total H_3 energy at the saddle point, and to obtain the classical barrier E_b to the $H + H_2$ exchange reaction. We perform Monte Carlo calculations for both spin-restricted and spin-unrestricted, single determinant, double-zeta-quality trial functions. Despite the simplicity of these Ψ_T 's, we obtain

in excess of 99% of the correlation energy, and determine E_b to an accuracy comparable to Liu's best result. To place this finding in perspective, in Sec. II we first give a brief description of the QMC approach and its history. In Sec. III we contrast spin-restricted and spin-unrestricted trial functions, both from the variational and the QMC points of view. Our results on the H_3 barrier are then presented and discussed in Sec. IV.

II. Quantum Monte Carlo

In recent years, Monte Carlo methods have been increasingly applied to quantum-mechanical problems. Such quantum Monte Carlo (QMC) methods fall into two major categories. Variational QMC [7] enables one to evaluate expectation values of physical quantities with a given trial wave function Ψ_T , which may be variationally optimized. In effect one evaluates a ratio of two integrals, although implementation of the Monte Carlo procedure is generally more sophisticated. On the other hand, "exact" QMC [6,8] is an approach in which the Schrödinger equation is directly solved numerically. Thus it is not necessary in the latter approach to already have a highly accurate wave function in order to compute reliable expectation values. Instead, a simulation of the quantum system is allowed to evolve under what is essentially the time-dependent Schrödinger equation (in imaginary time). After a stationary state is obtained, the properties of interest are "measured"; averages over this equilibrium state give the desired expectation values. Only recently have chemical calculations by exact QMC methods been carried out [6,9].

Exact QMC approaches differ slightly from one another [8]. The method we use here--the fixed-node, diffusion QMC--is outlined below. For a full discussion the reader is referred to Refs. [6b] and [8d].

Note first that the steady-state solution to the following equation,

$$-\frac{\partial \Psi(\underline{R}, t)}{\partial t} = [-D\nabla^2 + V(\underline{R}) - E_T] \Psi(\underline{R}, t) \quad (1)$$

is the solution to the time-independent Schrödinger equation. For a molecular system within the Born-Oppenheimer approximation, $D = \hbar^2/2m_e$, \underline{R} is the three-N dimensional coordinate vector of the N electrons, and $V(\underline{R})$ is the molecular Coulomb potential. Equation (1), however, is simply a diffusion equation combined with a first-order rate process, and thus may be readily simulated. This connection between a quantum system and a "random walk" was first noted by Metropolis who attributes it to Fermi [10]. The function $\Psi(\underline{R}, t)$ plays the role of the density of diffusing particles, which undergo exponential birth/death according to the rate term $[E_T - V(\underline{R})] \Psi(\underline{R}, t)$, and diffusion with a diffusion constant D.

Unless constrained by symmetry, the steady-state solution to Eq. (1) is the ground-state eigenfunction $\phi_0(\underline{R})$. Furthermore, the value of E_T at which the population of diffusers is asymptotically constant gives the energy eigenvalue E_0 [6]. The lowest eigenstate, however, is that of a Bose system. In order to treat a Fermi system, such as a molecule, one needs to impose anti-symmetry on $\Psi(\underline{R})$. A method which does this, and at the same time provides more efficient sampling (thereby reducing statistical error) is importance sampling with an anti-symmetrized trial wave function Ψ_T [8b]. The zeroes (nodes) of Ψ_T

become absorbing boundaries for the diffusion process, maintaining the anti-symmetry.

To implement importance sampling, Eq. (1) is multiplied by Ψ_T , and is rewritten in terms of a new probability density $f(\underline{R}, t)$ given by

$$f(\underline{R}, t) \equiv \Psi_T(\underline{R}) \psi(\underline{R}, t) \quad . \quad (2)$$

The resultant equation for $f(\underline{R}, t)$ may be written as

$$\frac{\partial f}{\partial t} = D\nabla^2 f + [E_T - E_L(\underline{R})]f - D\nabla \cdot [fF_Q(\underline{R})] \quad . \quad (3)$$

The local energy $E_L(\underline{R})$, and the "quantum force" $F_Q(\underline{R})$ are simple functions of Ψ_T . In particular,

$$E_L(\underline{R}) \equiv H\Psi_T(\underline{R})/\Psi_T(\underline{R}) \quad (4a)$$

and

$$F_Q(\underline{R}) \equiv 2\nabla\Psi_T(\underline{R})/\Psi_T(\underline{R}) \quad . \quad (4b)$$

Equation (3), like Eq. (1) is a generalized diffusion equation, now with the addition of a drift term due to the presence of F_Q .

It is Eq. (3) that we solve stochastically. Using a short-time Green's function approach, the diffusers follow a "random walk" whose asymptotic distribution is given by the steady-state solution $f_\infty(\underline{R})$ of Eq. (3). Properties of interest (e.g., the energy) are measured during the latter (equilibrium) part of the "walk," and are thus averages over the distribution $f_\infty(\underline{R})$.

Earlier work with QMC [6,9a] demonstrated that for a number of 2-10 electron molecules, exceptionally accurate ground-state total energies could be obtained by this method. These energies were in every case more accurate than the best estimates obtained by ab initio CI procedures. For a method to be truly useful in chemistry, however, one needs also to be able to calculate accurate energy differences, such as binding energies and barriers to chemical reaction. For QMC this is a far more difficult task, since a statistical uncertainty of 0.1% in the total energy can totally mask the sought after energy difference. Nevertheless, this problem is not insurmountable. First, one can proceed by "brute force" recognizing that as the sample size N increases the statistical error decreases as $1/\sqrt{N}$. This approach, however, extracts a great cost in computer time. On the other hand, algorithmic developments, such as the "differential QMC" [11] enable a reduction in statistical error by at least an order of magnitude through a correlated sampling technique.

In order that the solutions to Eq. (3) be antisymmetric, we impose the "fixed-node approximation." That is, we solve the Schrödinger equation subject to the boundary condition that $\Psi(\underline{R},t)$ vanish at the nodes of $\Psi_T(\underline{R})$. The magnitude of the error thus introduced depends on the quality of the nodes of $\Psi_T(\underline{R})$, and vanishes as $\Psi_T(\underline{R}) \rightarrow \phi_0(\underline{R})$. To the extent that $\Psi_T(\underline{R})$ is a good approximation to $\phi_0(\underline{R})$, the exact eigenfunction $\phi_0(\underline{R})$ is almost certainly quite small near the nodes of Ψ_T . Thus one expects the fixed-node error also to be small for a reasonable choice $\Psi_T(\underline{R})$. (In the present study this error is estimated to be no more than a few tenths of a kcal/mole.) Furthermore, this error is variationally bounded [6,8d].

But what is a "reasonable" choice of $\Psi_T(R)$? In practice one wants a trial function which is as simple as possible, and yet provides accurate results. Anderson's early work with the "random-walk method" [6a] had no importance sampling--corresponding to choosing $\Psi_T(R) \equiv 1$. Since even that exceptionally simple choice led to reasonable results, we feel confident using simple quantum chemical trial functions in this study.

III. Spin-restricted versus Unrestricted Trial Functions

In a self-consistent field (SCF) approach, it is well known that an unrestricted wave function $\Psi_{SCF}^{(u)}$ will have a lower energy expectation value than a restricted function $\Psi_{SCF}^{(r)}$. If allowing different coefficients for the up and down molecular spin-orbitals does not provide a reduction in energy, at worst the unrestricted SCF energy minimum will coincide with the restricted SCF energy. Thus,*

$$E_{\text{var}}^{(u)} \leq E_{\text{var}}^{(r)} \quad (5a)$$

where

$$E_{\text{var}}^{(i)} \equiv \langle \Psi_{SCF}^{(i)} | H | \Psi_{SCF}^{(i)} \rangle, \quad i = u, r \quad (5b)$$

A similar statement about the ordering of the corresponding fixed-node QMC energies--obtained using $\Psi_{SCF}^{(u)}$ and $\Psi_{SCF}^{(r)}$ as the trial functions--does

*Here $\Psi_{SCF}^{(u)}$ and $\Psi_{SCF}^{(r)}$ refers to a pair of variationally optimized functions, differing only by spin restriction. Our $\Psi_T^{(u)}$ and $\Psi_T^{(r)}$ in Sec. IV are SCF functions multiplied by Jastrow factors, without full re-optimization. Thus, Eq. (5a) need not hold for those Ψ_T 's.

not follow. The QMC energies are determined by the position of the nodes of Ψ_T , which are not necessarily optimized by optimizing E_{var} . A trial function with better nodes will give a lower QMC energy. In fact, a trial function with the exact nodes of $\phi_0(\mathbf{R})$ will give the exact energy, even if $\Psi_T(\mathbf{R})$ differs from $\phi_0(\mathbf{R})$ everywhere else. So the question becomes, does $\Psi_{\text{SCF}}^{(r)}$ or $\Psi_{\text{SCF}}^{(u)}$ provide the better nodal description of ϕ_0 ?

To answer this question, we need first to understand what we mean here by the nodes of a trial function. To this end we consider the SCF wave function Ψ_{SCF} and focus on the H_3 system. We begin with

$$\Psi_{\text{SCF}}(\mathbf{R}) = \begin{vmatrix} \psi_1(r_1)\alpha_1 & \psi_1(r_2)\alpha_2 & \psi_1(r_3)\alpha_3 \\ \psi_2(r_1)\beta_1 & \psi_2(r_2)\beta_2 & \psi_2(r_3)\beta_3 \\ \psi_3(r_1)\beta_1 & \psi_3(r_2)\beta_2 & \psi_3(r_3)\beta_3 \end{vmatrix} \quad (6a)$$

$$\begin{aligned} &= \psi_1(r_1) \begin{vmatrix} \psi_2(r_2) & \psi_2(r_3) \\ \psi_3(r_2) & \psi_3(r_3) \end{vmatrix} \alpha_1\beta_2\beta_3 \\ &- \psi_1(r_2) \begin{vmatrix} \psi_2(r_1) & \psi_2(r_3) \\ \psi_3(r_1) & \psi_3(r_3) \end{vmatrix} \alpha_2\beta_1\beta_3 \\ &+ \psi_1(r_3) \begin{vmatrix} \psi_2(r_1) & \psi_2(r_2) \\ \psi_3(r_1) & \psi_3(r_2) \end{vmatrix} \alpha_3\beta_1\beta_2 \end{aligned} \quad (6b)$$

The three terms in (6b) are equivalent. Each corresponds to having the electron in molecular orbital (MO) ψ_1 with spin up, and the electrons in MO's ψ_2 and ψ_3 with spin down. They differ only in the labels given the three electrons. For example, only the first term corresponds to assigning the up spin the label "1". Thus, in QMC where the spins are labelled, we need only consider one term in (6b). The other terms are sampled when the electrons are at these other coordinates. Thus we write

$$\Psi_{\text{SCF}}(\tilde{R}) = \psi_1(r_1) \begin{vmatrix} \psi_2(r_2) & \psi_2(r_3) \\ \psi_3(r_2) & \psi_3(r_3) \end{vmatrix} \alpha_1 \beta_2 \beta_3 \quad (7)$$

This function, unlike the general form Eq. (6), vanishes when a pair of particles (2 and 3) are in the same position. It is the nodes of a trial function in the form of Eq. (7) which determines the ultimate accuracy of the fixed-node QMC results.

We are now in a position to return to our discussion of the SCF functions $\Psi_{\text{SCF}}^{(r)}$ and $\Psi_{\text{SCF}}^{(u)}$. Let λ be the lowest MO of symmetry σ_g , and let μ be the lowest MO of symmetry σ_u . For H_3 we can write

$$\Psi_{\text{SCF}}^{(r)}(\tilde{R}) = \lambda(r_1) \begin{vmatrix} \lambda(r_2) & \lambda(r_3) \\ \mu(r_2) & \mu(r_3) \end{vmatrix} \alpha_1 \beta_2 \beta_3, \quad (8a)$$

and

$$\Psi_{\text{SCF}}^{(u)}(\tilde{R}) = \bar{\lambda}(r_1) \begin{vmatrix} \bar{\lambda}(r_2) & \bar{\lambda}(r_3) \\ \bar{\mu}(r_2) & \bar{\mu}(r_3) \end{vmatrix} \alpha_1 \beta_2 \beta_3 \quad (8b)$$

where λ , $\bar{\lambda}$, $\underline{\lambda}$, and μ and $\underline{\mu}$ differ in their parameter values. Although it is not clear which of Eqs. (8a) and (8b) has better nodes—i.e., nodes that more closely approximate the true H_3 solution—we can define a third function $\Psi_T'(r)$ which is spin-restricted and has the same nodes as $\Psi_{SCF}^{(u)}$:

$$\Psi_T'(r) \equiv \underline{\lambda}(r_1) \begin{vmatrix} \bar{\lambda}(r_2) & \bar{\lambda}(r_3) \\ \underline{\mu}(r_2) & \underline{\mu}(r_3) \end{vmatrix} \alpha_1 \beta_2 \beta_3. \quad (8c)$$

The nodes of $\Psi_T'(r)$ and $\Psi_{SCF}^{(u)}$ are the same because the MO $\bar{\lambda}$ is σ_g , and thus has no nodes of its own. Therefore, we have a restricted trial function $\Psi_T'(r)$ with the same QMC energy as $\Psi_{SCF}^{(u)}$, but with a higher variational energy than either $\Psi_{SCF}^{(u)}$ or $\Psi_{SCF}^{(r)}$ (since these latter wave functions are variationally optimized). Hence,

$$E_{\text{var}}^{(u)} \leq E_{\text{var}}^{(r)} \leq E_{\text{var}}'^{(r)} \quad (9a)$$

while

$$E_{\text{QMC}}^{(u)} = E_{\text{QMC}}'^{(r)}, \quad (9b)$$

where $E_{\text{var}}'^{(r)} = \langle \Psi_T'(r) | H | \Psi_T'(r) \rangle$, and $E_{\text{QMC}}^{(u)}$, $E_{\text{QMC}}^{(r)}$, and $E_{\text{QMC}}'^{(r)}$ are the QMC energies corresponding to the trial functions $\Psi_{SCF}^{(u)}$, $\Psi_{SCF}^{(r)}$ and $\Psi_T'(r)$.

Equation (9b) does not order $E_{\text{QMC}}^{(r)}$. There are thus two possibilities:

Case I: $E_{\text{QMC}}^{(r)} < E_{\text{QMC}}^{(u)}$. This case, at first glance seems counter-intuitive. Releasing the symmetry restriction on the spin orbitals should not raise the energy.

Case II: $E_{\text{QMC}}^{(r)} > E_{\text{QMC}}^{(u)}$. If this were the case, an equally seeming counter-intuitive result ensues. From (9b) we then obtain $E_{\text{QMC}}^{(r)} > E_{\text{QMC}}^{(r)}$. That is, comparing two spin-restricted functions, the optimized (SCF) function $\Psi_{\text{SCF}}^{(r)}$ has a higher energy than the function we defined in (8c).

In reality there is no problem with either case, since the SCF optimization does not imply a QMC optimization. In fact, an optimization for the lowest QMC energy would result (in the case of H_3) in an unrestricted function having the same QMC energy as an optimized restricted function. This follows from Eq. (8), since only the 2×2 determinant determines the nodes for both the restricted and unrestricted forms of Ψ_{T} .

Using variational (SCF) optimization for Ψ_{T} , QMC computations* (see next section) are found to yield a lower energy for the restricted function $\Psi_{\text{SCF}}^{(r)}(\tilde{R})$, i.e., Case I. In other words, $\Psi_{\text{SCF}}^{(r)}(\tilde{R})$ provides, in this case, the better nodal description of $\phi_0(\tilde{R})$. Our numerical results are presented and discussed below.

IV. H_3 Saddle Point

Recently, Liu [4] has performed extensive ab initio configuration interaction (CI) calculations, with extended Slater-type basis sets, on H_3 at the saddle point geometry. That work provides a benchmark against

*Our actual $\Psi_{\text{T}}(\tilde{R})$ contains additional factors (cf., Sec. IV), but as these are purely positive the nodes of Ψ_{T} and hence the QMC energy are unaffected.

which the QMC approach might be judged. Here we report on a QMC calculation of H_3 using essentially a double-zeta STO basis set (see Table I), at the collinear saddle point geometry [3] $R_{ab} = R_{bc} = 1.757$ bohr, where $R_{\alpha\beta}$ is the internuclear separation. We discuss results obtained with single-determinant spin-restricted and unrestricted SCF functions $\Psi_{SCF}^{(r)}$ and $\Psi_{SCF}^{(u)}$. These functions are multiplied by electron-electron and electron-nuclear Jastrow factors [12,6b,9b,c]. Since these factors are positive definite, they do not affect the position of the nodes, and therefore leave the QMC energy invariant. These terms do, however, speed the convergence of the Monte Carlo energy estimate, by making $E_L(\underline{R})$ a smoother function. Of course, by introducing correlation, the Jastrow factors lower the variational energies obtained from the product functions $\Psi_T^{(r)}$ and $\Psi_T^{(u)}$ vis a vis the SCF energy.

Our QMC results for the saddle-point energy E_{sp} , and the barrier E_b are presented in Table II. They are compared with the Hartree-Fock energy, Liu's CI calculation and the variational energies obtained from $\Psi_{SCF}^{(r)}$, $\Psi_{SCF}^{(u)}$, and $\Psi_T^{(r)}$ and $\Psi_T^{(u)}$. These variational energies, given in lines 2-5, give an indication of the quality of the trial functions as compared to the CI wave function. Note that although the bounded barrier height obtained variationally with $\Psi_T^{(r)}$ is roughly three times too large, this same function in the fixed-node QMC approach gives a bound of $E_b = 9.69 \pm 0.25$ kcal/mole, whose mean is lower than Liu's CI result, and is within 0.1 kcal/mole of the presumed exact result. The fixed-node QMC approach gives a bounded energy since the

ground-state energies of both H and H_2 are given exactly by QMC [6]. We also note that, as discussed in Sec. III, the SCF function $\Psi_{SCF}^{(u)}$ gives a poorer description of the nodes of ϕ_0 than the spin-restricted SCF function $\Psi_{SCF}^{(r)}$. This is evidenced by a higher QMC energy.

Recently, Anderson's group [13] and Ceperley [14] have independently also performed QMC calculations on the H_3 system. Using planar nodes in their trial functions, both groups obtain $E_b = 10.2 \pm 0.2$ kcal/mole. Ceperley also "releases the nodes", enabling the system to relax to its exact Fermi ground state. His answer of 9.68 ± 0.08 kcal/mole is in good agreement with the present results.

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Table Captions

Table I. The self-consistent field trial functions $\psi_{\text{SCF}}^{(r)}$ and $\psi_{\text{SCF}}^{(u)}$ used in this paper [cf., Eq. (7)]. The molecular geometry is collinear, with $R_{ab} = R_{bc} = 1.757$ bohr. The outer H atoms have a double-zeta basis set. To limit the number of basis functions, the central atom has a single 1s function with an optimized zeta.

Table II. Comparison of saddle-point energies and barrier heights for $\text{H} + \text{H}_2$. A restricted and unrestricted SCF trial function are contrasted. The functions $\psi_{\text{SCF}}^{(r)}$ and $\psi_{\text{SCF}}^{(u)}$ are described in Table I; $\psi_{\text{T}}^{(r)}$ and $\psi_{\text{T}}^{(u)}$ have additional Jastrow factors. The last two lines of the table give the fixed-node QMC energies. The best QMC energies are lower than the best CI results.

Table I

| Trial Function | STO | <u>Molecular Orbitals</u> | | | |
|------------------------|------------|---------------------------|----------|----------|----------|
| | | ζ | ψ_1 | ψ_2 | ψ_3 |
| $\psi_{\text{SCF}}(r)$ | $1s_{a,1}$ | 1.275 | 0.30377 | 0.30377 | 0.02016 |
| | $1s_{a,2}$ | 0.925 | 0.01525 | 0.01525 | 0.82413 |
| | $1s_b$ | 1.120 | 0.58878 | 0.58878 | 0 |
| | $1s_{c,1}$ | 1.275 | 0.30377 | 0.30377 | -0.02016 |
| | $1s_{c,2}$ | 0.925 | 0.01525 | 0.01525 | -0.82413 |
| $\psi_{\text{SCF}}(u)$ | $1s_{a,1}$ | 1.250 | 0.26704 | 0.39079 | 0.06092 |
| | $1s_{a,2}$ | 0.925 | -0.03444 | 0.01129 | 0.78015 |
| | $1s_b$ | 1.120 | 0.71417 | 0.45952 | 0 |
| | $1s_{c,1}$ | 1.250 | 0.26704 | 0.39079 | -0.06092 |
| | $1s_{c,2}$ | 0.925 | -0.03444 | 0.01129 | -0.78015 |

Table II

| Method | Total Saddle-Point Energy E_{sp} (hartrees) | Bounded Barrier Height $E_{sp} - [E(H) + E(H_2)]_{exact}$ (kcal/mole) | Estimated Barrier Height E_b (kcal/mole) |
|---|---|---|--|
| Hartree-Fock | -1.59465 ^a | 50.1 | 24.5 ^a |
| $\langle \psi_{SCF}^{(r)} H \psi_{SCF}^{(r)} \rangle$ | -1.5893 | 53.4 | - |
| $\langle \psi_{SCF}^{(u)} H \psi_{SCF}^{(u)} \rangle$ | -1.5995 | 47.0 | - |
| $\langle \psi_T^{(r)} H \psi_T^{(r)} \rangle$ | -1.6323(20) | 26.5(1.3) | - |
| $\langle \psi_T^{(u)} H \psi_T^{(u)} \rangle$ | -1.6309(4) | 27.4(0.2) | - |
| Best CI | -1.65876 ^b | 9.86 ^b | 9.59(0.06) ^b |
| QMC($\psi_T^{(u)}$) | -1.65822(41) | 10.20(0.26) | - |
| QMC($\psi_T^{(r)}$) | -1.65903(40) | 9.69(0.25) | - |

a Derived from Ref. 3 by third order fit to H₃ SCF surface.

b Ref. 4

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