

Improved Nonadiabatic Ground-State Energy Upper Bound for Dihydrogen

Donald B. Kinghorn and Ludwik Adamowicz

Department of Chemistry, University of Arizona, Tucson, Arizona 85721

(Received 21 April 1999)

A new, highly accurate, value for the nonadiabatic energy of the dihydrogen ground state is reported, ($-1.164\,025\,023\,2$ hartree). The calculations were performed with a direct nonadiabatic variational approach using a new correlated Gaussian basis set including powers of the internuclear distance.

PACS numbers: 31.15.Pf, 31.25.Nj, 31.30.-i

We recently introduced a new correlated Gaussian basis set suitable for high accuracy nonadiabatic calculations on diatomic molecules [1]. In that paper we gave a detailed description of the basis set including formulas for matrix elements and energy gradient components together with information on implementation. We demonstrated the implementation by including accurate results for the standard reference system H_2^+ . In this Letter we continue the validation of this new basis by reporting a new variational energy upper bound for the ground state of dihydrogen molecule. This new bound should provide an accurate reference energy for future nonadiabatic calculations and for evaluating the quality of adiabatic plus nonadiabatic "correction" methodologies that are based on the Born-Oppenheimer approximation.

In the nonadiabatic approach all particles are treated equally utilizing their given masses and full interactions with all other particles. Without invoking any approximations, the total Hamiltonian can be separated into an operator representing the translational motion of the center of mass and an operator representing the internal energy. We perform this separation by making a transformation to an internal reference frame with origin at particle one,

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \end{bmatrix} = \begin{bmatrix} \mathbf{R}_2 - \mathbf{R}_1 \\ \mathbf{R}_3 - \mathbf{R}_1 \\ \mathbf{R}_4 - \mathbf{R}_1 \end{bmatrix}, \quad (1)$$

where the \mathbf{R}_i are the original particle coordinates. This transformation to internal coordinates together with the conjugate momentum transformation yields the nonadiabatic Hamiltonian for the internal energy of a four particle system,

$$H = -\frac{1}{2} \left(\sum_i^3 \frac{1}{\mu_i} \nabla_i^2 + \sum_{i \neq j}^3 \frac{1}{M_1} \nabla_i' \nabla_j' \right) + \sum_{i=1}^3 \frac{q_0 q_i}{r_i} + \sum_{i < j}^3 \frac{q_i q_j}{r_{ij}}. \quad (2)$$

Here the μ_i are reduced masses, M_1 is the mass of particle 1 (the coordinate reference particle), and ∇_i is the gradient with respect to the x, y, z coordinates \mathbf{r}_i . The potential energy is the same as in the total Hamiltonian but is now written using internal distance coordinates. The charges are mapped from the original

particles as $\{Q_1, Q_2, Q_3, Q_4\} \mapsto \{q_0, q_1, q_2, q_3\}$. In internal coordinates, distances are denoted (using the standard 2-norm) $r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\| = \|\mathbf{R}_{i+1} - \mathbf{R}_{j+1}\|$ with $r_j = \|\mathbf{r}_j\| = \|\mathbf{R}_{j+1} - \mathbf{R}_1\|$. More general information on the nonadiabatic Hamiltonian and the center of mass transformation can be found in Ref. [1].

The basis set consists of explicitly correlated Gaussian's multiplied by powers of the internuclear distance. The general form is ($'$ represents vector/matrix transposition and \otimes is the Kronecker product symbol)

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \quad (3)$$

where, for H_2 , \mathbf{r} is a 9×1 vector of internal Cartesian coordinates, L_k is an 3×3 rank 3 lower triangular matrix of nonlinear variation parameters, and I_3 is the 3×3 identity matrix. The Kronecker product with the identity ensures rotational invariance of the basis functions (the ϕ_k are angular momentum eigenfunctions with $J = 0$). The exponent parameters are written in Cholesky factored form, $L_k L_k'$, to ensure positive definiteness of the quadratic form in the exponential, thereby ensuring L^2 integrability of the basis functions. For a more complete discussion of this basis and derivation of the Hamiltonian matrix elements and derivatives in matrix form, see Ref. [1].

Basis functions for the ground-state wave function are obtained by symmetry projecting the ϕ_k using a projection operator \mathcal{P} . Thus,

$$\mathcal{P} \phi_k = \sum_P \chi_P r_1^{m_k} \exp[-\mathbf{r}'(\tau_P' A_k \tau_P \otimes I_3)\mathbf{r}], \quad (4)$$

where τ_P are the permutation matrices transforming the internal coordinates,

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \begin{pmatrix} -1 & 0 & 0 \\ -1 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix}, \quad (5)$$

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \begin{pmatrix} -1 & 0 & 0 \\ -1 & 0 & 1 \\ -1 & 1 & 0 \end{pmatrix}.$$

The coefficients χ_P are from the matrix elements of the irreducible representation for the desired state, and for the ground state are all ones.

TABLE I. Energy expectation value for the dihydrogen nonadiabatic ground state using a 512 term correlated Gaussian wave function and comparison with literature values are shown. Energy is given in hartrees.

-1.164 025 023 2	This work (H mass = 1836.152 693 a.u.); variational, 512 basis functions
-1.164 025 018	Wolniewicz Ref. [8] (H mass = 1836.1527; high accuracy adiabatic and nonadiabatic corrections)
-1.164 024 13	Bishop and Cheung Ref. [9] (H mass = 1836.15 a.u.); variational, 1070 basis functions
-1.164 023 9	Chen and Anderson Ref. [10] (H mass not given); quantum Monte Carlo

The hydrogen nuclear mass was computed using the atomic mass given in *The 1993 atomic mass evaluation* of Audi and Wapstra [2], 1836.152 693 a.u. This value is derived from the hydrogen atom atomic mass by correcting for the electron mass and the binding energy of the electron. We also performed calculations using the proton mass from the CODATA [3] proton electron mass ratio 1836.152 701(37) a.u. This slightly larger mass value lowered the energy by 2 units in the 11th decimal digit. However, we prefer to use the nuclear mass derived from the atomic mass and report only those values. We use quantum units in this work except where otherwise noted. Thus, $\hbar = 1$, $m_e = 1$, energy is in hartree ($= 2R_\infty$), and distance is in bohr.

The wave function for the ground state is obtained by minimizing the Rayleigh quotient;

$$E(a; c) = \min_{(a,c)} \frac{c'H(a)c}{c'S(a)c}, \quad (6)$$

where $H(a)$ and $S(a)$ are the Hamiltonian and overlap matrices, respectively, which are functions of the nonlinear parameters contained in the basis set exponent matrices L_k . We write a for the collection of these nonlinear parameters and c is the vector of linear coefficients in the basis expansion of the wave function. Our experience indicates that much more thorough optimization can be achieved by letting the optimizer simultaneously vary both the linear and nonlinear parameters in the Rayleigh quotient rather than alternately solving the eigenproblem for the c 's and only letting the optimizer vary the nonlinear parameters a . The optimization software employed was the package TN by Stephen Nash [4]—available from netlib [5]. TN is a truncated Newton method utilizing a user supplied gradient. The analytic gradient of

the energy functional was derived using matrix differential calculus [6,7] and is given in Ref. [1].

Starting values for the wave function parameters (exponent matrices, L_k , and powers of the internuclear distance, m_k) were first obtained for small wave functions by random trials. Larger wave functions were then built from optimized parameters obtained from smaller wave function and then reoptimized. The optimal single value for powers, m_k , was found to be 18. The larger wave functions have values of m_k ranging from 0 to 26 with the majority of values set at 16, 18, and 20.

Tables I and II contain expectation values computed using our optimized nonadiabatic wave functions. In Table I the energy expectation value using a wave function consisting of 512 basis functions ϕ_k is given along with the available literature values for comparison. Included in Table II are expectation values for the Hamiltonian, $\langle H \rangle$, the kinetic, $\langle T \rangle$, and potential energy, $\langle V \rangle$, the virial coefficient $\eta = -\langle V \rangle / 2\langle T \rangle$, the squared norm of the energy gradient, $\|g\|_2^2$, and r_1 and r_1^2 computed using wave functions with from 64 to 512 basis functions. This table demonstrates the rather remarkable convergence of this basis set. The values of the virial coefficient and the gradient norm indicate the high level of optimization obtained for these wave functions. The energy we report for the nonadiabatic ground state of H_2 is a new rigorous variational upper bound.

Our current development efforts involve generalizing the basis for polyatomic systems and writing parallel software to handle the arduous task of optimizing many nonlinear parameters. With this parallel implementation we will be able to perform direct nonadiabatic calculations on systems with more than two nuclei. No one has yet carried out such calculations.

TABLE II. Expectation values are shown for the dihydrogen nonadiabatic ground state using correlated Gaussian wave functions with from 64 to 512 basis functions. Energy is given in hartrees, distance in bohr. (H mass = 1836.152 693 a.u.)

N	64	128	256	512
$\langle H \rangle$	-1.164 017 767 8	-1.164 024 473 5	-1.164 024 964 3	-1.164 025 023 2
$\langle T \rangle$	1.164 017 816 4	1.164 024 508 4	1.164 024 902 4	1.164 025 004 1
$\langle V \rangle$	-2.328 035 584 1	-2.328 048 981 9	-2.328 049 866 7	-2.328 050 027 3
η	0.999 999 979 1	0.999 999 985 0	1.000 000 026 5	1.000 000 008 1
$\ g\ _2^2$	5.552×10^{-15}	9.981×10^{-15}	1.008×10^{-14}	4.074×10^{-15}
$\langle r_1 \rangle$	1.448 699 152 8	1.448 735 462 2	1.448 737 805 8	1.448 738 000 1
$\langle r_1^2 \rangle$	2.126 838 127 4	2.127 033 468 7	2.127 044 974 9	2.127 045 959 5

This work was supported by the National Science Foundation.

-
- [1] D. B. Kinghorn and L. Adamowicz, *J. Chem. Phys.* **110**, 7166 (1999).
- [2] G. Audi and A. H. Wapstra, *Nucl. Phys.* **A565**, 1 (1993).
- [3] See CODATA database of fundamental constants at <http://www.codata.org>.
- [4] S. G. Nash, *SIAM J. Numer. Anal.* **21**, 770 (1984).
- [5] netlib can be accessed by ftp at netlib@ornl.gov and netlib@research.att.com or by World Wide Web access at <http://www.netlib.org>.
- [6] D. B. Kinghorn, *Int. J. Quantum Chem.* **57**, 141 (1996).
- [7] D. B. Kinghorn and R. D. Poshusta, *Int. J. Quantum Chem.* **2**, 223 (1997).
- [8] L. Wolniewicz, *J. Chem. Phys.* **103**, 1792 (1995).
- [9] D. M. Bishop and L. M. Cheung, *Phys. Rev. A* **18**, 1846 (1978).
- [10] B. Chen and J. B. Anderson, *J. Chem. Phys.* **102**, 2802 (1995).