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A new, highly accurate, value for the non-adiabatic energy of the dihydrogen ground state is reported, (-1.1640250232 hartree). The calculations were performed with a direct non-adiabatic variational approach using a new correlated Gaussian basis set including powers of the the inter-nuclear distance.

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We recently introduced a new correlated Gaussian basis set suitable for high accuracy non-adiabatic 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  $\text{H}_2^+$ . 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 non-adiabatic calculations and for evaluating the quality of adiabatic plus non-adiabatic “correction” methodologies that are based on the Born-Oppenheimer approximation.

In the non-adiabatic 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 non-adiabatic 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  $\mu_i$  are reduced masses,  $M_1$  is the mass of particle 1, (the coordinate reference particle), and  $\nabla_i$  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 non-adiabatic Hamiltonian and the center of mass transformation can be found in the references [1].

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

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}' (\mathbf{L}_k \mathbf{L}_k' \otimes \mathbf{I}_3) \mathbf{r}], \quad (3)$$

where, for  $\text{H}_2$   $\mathbf{r}$  is a  $9 \times 1$  vector of internal Cartesian coordinates,  $L_k$  is an  $3 \times 3$  rank 3 lower triangular matrix of nonlinear variation parameters, and  $I_3$  is the  $3 \times 3$  identity matrix. The Kronecker product with the identity insures rotational invariance of the basis functions (the  $\phi_k$  are angular momentum eigen-functions with  $J=0$ ). The exponent parameters are written in Cholesky factored form,  $L_k L_k'$ , to insure positive definiteness of the quadratic form in the exponential thereby, insuring  $L^2$  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 reference [1].

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

$$\mathcal{P}\phi_k = \sum_P \chi_P r_1^{m_k} \exp[-\mathbf{r}' (\tau_P' \mathbf{A}_k \tau_P \otimes \mathbf{I}_3) \mathbf{r}], \quad (4)$$

where  $\tau_P$  are the permutation matrices transforming the internal coordinates,

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

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

The hydrogen nuclear mass was computed using the atomic mass given in *The 1993 atomic mass evaluation* of Audi and Wapstra [2], 1836.152693a.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 1836.152701(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 wavefunction. 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 eigen-problem 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 the references [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 re-optimized. 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 non-adiabatic wave functions. In table (I) the energy expectation value using a wave function consisting of 512 basis functions,  $\phi_k$  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 non-adiabatic 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 non-adiabatic calculations on systems with more than two nuclei. No-one has yet carried out such calculations.

## ACKNOWLEDGMENTS

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TABLE I. Energy expectation value for the dihydrogen non-adiabatic ground state using a 512 term correlated Gaussian wave function. Comparison with literature values. Energy in Hartree.

|               |   |
|---------------|---|
| -1.1640250232 | This work (H mass= 1836.152693a.u.)<br>Variational, 512 basis functions                           |
| -1.164025018  | Wolniewicz ref. [8], (H mass= 1836.1527)<br>High accuracy adiabatic and non-adiabatic corrections |
| -1.16402413   | Bishop and Cheung ref. [9],(H mass= 1836.15a.u)<br>Variational, 1070 basis functions              |
| -1.1640239    | Chen and Anderson ref. [10],(H mass not given)<br>Quantum Monte Carlo                             |

TABLE II. Expectation values for the dihydrogen non-adiabatic ground state using correlated Gaussian wave functions with from 64 to 512 basis functions. Energy in Hartree, distance in Bohr. (H mass= 1836.152693a.u.)

| $N$                     | 64                      | 128                     | 256                     | 512                     |
|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| $\langle H \rangle$     | -1.1640177678           | -1.1640244735           | -1.1640249643           | -1.1640250232           |
| $\langle T \rangle$     | 1.1640178164            | 1.1640245084            | 1.1640249024            | 1.1640250041            |
| $\langle V \rangle$     | -2.3280355841           | -2.3280489819           | -2.3280498667           | -2.3280500273           |
| $\eta$                  | 0.9999999791            | 0.9999999850            | 1.0000000265            | 1.0000000081            |
| $\ g\ _2^2$             | $5.552 \times 10^{-15}$ | $9.981 \times 10^{-15}$ | $1.008 \times 10^{-14}$ | $4.074 \times 10^{-15}$ |
| $\langle r_1 \rangle$   | 1.4486991528            | 1.4487354622            | 1.4487378058            | 1.4487380001            |
| $\langle r_1^2 \rangle$ | 2.1268381274            | 2.1270334687            | 2.1270449749            | 2.1270459595            |