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Non-Born–Oppenheimer calculations on the LiH molecule with explicitly correlated Gaussian functions

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We report the first ever non-Born–Oppenheimer variational calculations on the ground state of a four electron molecular system. The basis set used in the calculations consists of explicitly correlated Gaussians multiplied by powers of the internuclear distance. To accelerate the optimization of the many nonlinear variational parameters involved in the variational wave function, we performed the calculations on a cluster of Linux workstations using MPI and a parallel implementation of the formulas. Results for the nonadiabatic ground state energy of LiH, as well as expectation values for the kinetic and potential energies, the internuclear and square of the internuclear distance, the virial coefficient, and the square of the energy gradient norm are reported. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1342757]

I. INTRODUCTION

Basis sets comprised of one-center explicitly correlated Gaussians (ECG), exponentially dependent on the squares of the interparticle distances, have been used successfully to calculate variational upper bounds for the nonadiabatic ground states of atomic and exotic few particle systems. Some systems studied include ^{4}He, Ps_2, and ^{9}Be (see Ref. 1). Efficient analytic formulas for the Hamiltonian matrix elements and the energy gradient have allowed for thorough optimization of the wave-functions. However, a shortcoming of the ECG basis set is its inability to describe the relative motion of two or more nuclei, making it unsuitable for calculations on molecular systems. This limitation suggests the use of correlated Gaussians with shifted centers. However, this is not straight forward in a non-Born–Oppenheimer approach because the shifted Gaussians do not reflect the fully symmetric nature of the non-Born–Oppenheimer Hamiltonian, though work is being done in our group to try and compensate for this deficiency. The approach taken in this paper is to augment the correlated Gaussian basis functions by the addition of premultiplying factors. The premultiplying factors used are powers of the squared internuclear distance. The addition of this factor accounts for the separation of the nuclei by shifting the probability density of one nucleus away from the other in the internal coordinate frame used in the nonadiabatic approach. With the addition of this premultiplying factor we have a basis set suitable for calculations on diatomic species, and great success was achieved in the calculations on the isotopomers of the hydrogen molecule[2] when this basis set was employed. In the present work results of calculations on the LiH molecule are presented. The additional electrons in this system significantly increase the computational effort required to perform sound non-Born–Oppenheimer calculations. To achieve the necessary processing power to run calculations on larger wave functions, we utilized a parallel implementation of the computer code on a four node cluster of dual-processor Linux workstations.

The details of this *N*-body correlated basis set, together with formulas for the Hamiltonian matrix elements and ananalytic gradient for the energy with respect to the nonlinear and linear parameters in the wave function, were previously reported by Kinghorn and Adamowicz.[3,4] Specifics on the nonadiabatic Hamiltonian, the transformation to internal coordinates, and the separation of the translational motion are also described there.

II. NONADIABATIC HAMILTONIAN

For a system of six particles with masses $\{M_1, \ldots, M_6\}$ and charges $\{Q_1, \ldots, Q_6\}$, interacting under a Coulombic potential, the nonrelativistic Hamiltonian is separable into a component describing the translational motion of the center-of-mass and a component describing the internal energy of the system. This separation is achieved by transforming from real particle coordinates $(\mathbf{R}_1, \ldots, \mathbf{R}_6)$ to center-of-mass $(\mathbf{r}_0)$ and internal coordinates $(\mathbf{r}_1, \ldots, \mathbf{r}_5)$:

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_0 \\ \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \\ \mathbf{r}_4 \\ \mathbf{r}_5 \end{bmatrix} = \begin{bmatrix} \mathbf{R}_{\text{c.o.m}} \\ \mathbf{R}_2 - \mathbf{R}_1 \\ \mathbf{R}_3 - \mathbf{R}_1 \\ \mathbf{R}_4 - \mathbf{R}_1 \\ \mathbf{R}_5 - \mathbf{R}_1 \\ \mathbf{R}_6 - \mathbf{R}_1 \end{bmatrix}, \tag{1}$$

where $\mathbf{R}_{\text{c.o.m.}}$ is the vector describing the center of mass of the system in the laboratory coordinate frame. The Hamiltonian describing the internal energy of the system is then given by

$$H_{\text{int}} = -\frac{1}{2} \left(\sum_{i=1}^{5} \frac{1}{\mu_i} \nabla_i^2 + \sum_{i \neq j}^{5} \frac{1}{M_1} \nabla_i' \nabla_j \right) + \sum_{i=1}^{5} \frac{q_0 q_i}{r_i} + \sum_{i<j}^{5} \frac{q_i q_j}{r_{ij}}, \tag{2}$$

where the μ_i are reduced masses, M_1 is the mass of particle 1 (the coordinate reference particle; usually the heaviest particle in the system), ∇_i is the gradient with respect to the x,y,z coordinates $\mathbf{r}_i$, and the r_{ij} are given by $r_{ij}=\|\mathbf{r}_i-\mathbf{r}_j\|$ $=\|\mathbf{R}_{i+1}-\mathbf{R}_{j+1}\|$. The prime ($'$) is used to denote vector/matrix transposition. The charges are mapped from the original particles as $\{Q_1,Q_2,Q_3,Q_4,Q_5,Q_6\}$ $\mapsto\{q_0,q_1,q_2,q_3,q_4,q_5\}$.

III. BASIS SET

In our calculations we used a basis of explicitly correlated Gaussians multiplied by powers of the internuclear distance. If we use $\otimes$ to denote the Kronecker product of two matrices, the general form for our basis functions is given by

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

where $\mathbf{r}$ is the 15×1 vector of internal Cartesian coordinates, L_k is a 5×5 lower triangular matrix containing the nonlinear parameters, I_3 is the 3×3 identity matrix, and m_k is an even integer number. The Kronecker product with the identity insures that these basis functions are rotationally invariant and hence are eigenfunctions of the angular momentum operator with $J=0$. By writing the matrix of nonlinear parameters in the Cholesky factored form, L_kL_k', we insure positive definiteness of the quadratic form in the exponential, which in turn insures square integrability of the basis functions. It should also be noted that r_1 refers to the internal coordinate representing the internuclear distance. For more information about this basis set the reader is referred to a previous paper.[2]

IV. SYMMETRY

The nonadiabatic Hamiltonian for a four electron system is invariant under the permutation group S_4 acting on the four electrons, and therefore eigenfunctions can be chosen which generate irreducible representations (I.R.) of S_4. In accordance with the antisymmetry principle we are interested only in those eigenfunctions which generate an antisymmetric representation. The LiH ground state is a singlet state, and from inspection of the four-electron branching diagram it is seen that the spin-component of the wave function must lie in a subspace generating a two-dimensional I.R. of S_4. The only two-dimensional I.R. of S_4 can be conveniently labeled by the Young frame

$$\begin{array}{|c|c|}\hline & \\\hline & \\\hline\end{array}.$$

The corresponding Young tableaux for this irreducible representation are

$$T_1=\begin{array}{|c|c|}\hline 1 & 2 \\\hline 3 & 4 \\\hline\end{array}\text{ and }T_2=\begin{array}{|c|c|}\hline 1 & 3 \\\hline 2 & 4 \\\hline\end{array}.$$

The spatial wave function with the proper symmetry will lie in a subspace generating the I.R. conjugate to the above representation. In this case the I.R. in question is self-conjugate, so both the spin and spatial components of the wave function must lie in subspaces forming bases for the same I.R. To form pure state eigenfunctions we must project this symmetry from the basis functions. Two suitable sym-

metry projectors can be obtained using the Young $E_{11}=P$ $\times N$ and $E_{12}=P\times N\times(23)$ operators, which are easily constructed from the above Young Tableaux,

$$E_{11}=P\times N$$
$$=[(E+(12))(E+(34))]\times[(E-(13))(E-(24))] \tag{4}$$

and

$$E_{12}=P\times N\times(23)$$
$$=[(E+(12))(E+(34))]$$
$$\times[(E-(13))((23)-(34))]. \tag{5}$$

The operator P is defined as $P=P_1P_2$, where P_i is the symmetrizer for the numbers standing in the ith row of T_1. N is an operator defined as $N=N_1N_2$, where the N_i are the antisymmetrizers for the numbers standing in the ith column of T_1. (23) is the permutation that changes the tableau T_1 into T_2.

In our implementation of symmetry only the projector E_{11} was used. Since our nonadiabatic approach includes transforming to internal coordinates, the matrix form of our projection operator is obtained from the operator expressed in the real particle frame by the appropriate transformation. Thus, if τ_P are the permutation matrices transforming the internal coordinates, the result of operator E_{11} acting on the basis function ϕ_k can be expressed as

$$\mathcal{P}\phi_k=\sum_P \chi_P\tau_P, \tag{6}$$

with the values of the coefficients χ_P derived from Eq. (4). The summation runs over all elements of the permutation group S_4. Thus the basis functions with the correct symmetry are then given by

$$\mathcal{P}\phi_k=\sum_P \chi_P r_1^{m_k}\exp[-\mathbf{r}'(\tau_P'L_kL_k'\tau_P\otimes I_3)\mathbf{r}]. \tag{7}$$

It should be noticed that the projection operator does not affect the internal coordinate r_1 because this coordinate is not an electron coordinate.

Calculating the matrix elements for these symmetry projected basis functions can be reduced by taking advantage of the commutation of the Hamiltonian with the elements of the permutation group S_4. Thus, since

$$\langle\mathcal{P}\phi_k|H|\mathcal{P}\phi_l\rangle=\langle\phi_k|H|\mathcal{P}^\dagger\mathcal{P}\phi_l\rangle, \tag{8}$$

the symmetry projection need only be performed on the ket.

V. MASS VALUES AND OTHER CONSTANTS

The nuclear masses were computed using the atomic masses published in *The 1993 atomic mass evaluation* of Audi and Wapstra,[5] H[1836.152693 a.u.], Li[12786.39354 a.u.]. These values are derived from the atomic masses by correcting for the electron mass and the binding energy of the electron. We use quantum units in this work except where otherwise noted. Thus, $\hbar=1$, $m_e=1$, energy is in hartrees, and distance is in bohr.

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VI. IMPLEMENTATION AND RESULTS

If we let a denote the collection of nonlinear parameters contained in the matrices L_k for a given trial function, then the Hamiltonian (H) and overlap (S) matrices will be functions of a, and the Rayleigh quotient is expressible as

$$E(a,c) = \min_{\{a,c\}} \frac{c'H(a)c}{c'S(a)c}, \qquad (9)$$

where c is the vector of the linear coefficients in the expansion of the wave function.

By allowing the optimization routine to vary both the linear and nonlinear parameters, rather than alternately solving the eigensystem and then varying the nonlinear parameters only, a much more thorough optimization is achieved. The optimization software employed was the TN package by Nash[6] available from netlib,[7] which is a truncated Newton method using a user supplied gradient. A derivation of the analytic gradient of $E(a,c)$ with respect to a and c was given in a previous paper.[4] It should be noted that the powers of the internuclear distance (m_k) are not optimized during energy minimization. The procedure used for their selection is described below.

Since the optimization is sensitive to the initial guesses for the nonlinear parameters, as well as the set of powers $\{m_k\}$ for the internuclear distance used in the wave function, a great deal of experimentation was carried out on smaller 8-term wave functions in order to gain some insight into how the set of powers $\{m_k\}$ should be chosen. In a series of calculations we performed on 8-term wave functions, randomly generated starting values for the nonlinear parameters were used, and the value m for the power of the internuclear distance was varied, so that each trial spatial wave function was of the form

$$\psi = \sum_{k=1}^{8} c_k r_1^m \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}], \qquad (10)$$

with m varying between 0 and 70. The results for values of m near the minimum are presented in Table I, where it is seen that the optimal value of m for 8-term wave functions is 58. For each value of m, only the best energy from many trials is shown.

With the results of Table I in mind, more calculations were run on smaller trial functions using a spectrum of values for m_k. Both the center and the degree of dispersion of the spectrum was varied. In this manner, larger wave functions were built from smaller ones using the combination of optimized nonlinear parameters and powers m_k that worked best. Eventually a reasonable idea of the optimal set of values $\{m_k\}$ for use in larger wave functions was determined. For the 512-term wave function values of m_k ranging from 0 to 70 were used, with the majority of values set near 56.

The values of m_k used for the trial function, together with the nonlinear parameters for r_1 in the exponentials, affect both the degree to which the probability density of the hydrogen nucleus is shifted away from the lithium nucleus, as well as the overall shape of the wave function in the r_1 coordinate. As the trial function is a linear sum of many basis functions, caution should be exercised in trying to

TABLE I. Calculated energies for 8-term wave functions of the form $\psi = \sum_{k=1}^{8} c_k r_1^m \exp[-\mathbf{r}'(L_k L_k' \otimes I_3)\mathbf{r}]$.

m	Energy in hartrees
34	−7.902 177 042 2
36	−7.929 739 227 5
38	−7.929 836 421 3
40	−7.897 209 220 1
42	−7.905 727 441 9
44	−7.912 512 075 6
46	−7.966 665 442 2
48	−7.966 700 651 5
50	−7.966 728 101 3
52	−7.966 748 665 1
54	−7.966 763 090 5
56	−7.966 772 021 0
58	−7.966 776 013 5
60	−7.966 775 552 2
62	−7.966 771 060 5
64	−7.966 762 910 1
66	−7.966 751 428 2

glean too much from the makeup of the set of powers m_k, but in general as the internuclear distance grows larger it is expected the optimal values for the m_k will shift to larger values. Also, when the equilibrium internuclear distance stays the same, but the masses of the nuclei increase and the vibrational wave function becomes more localized, the m_k will shift to larger values. This effect was observed in our previous calculations on the isotopomers of the hydrogen molecule,[1] where the ''optimal'' values of m_k shifted from 18 for H_2 to 34 for T_2.

The overall shape of the wave function in the coordinate r_1 should be reflective of the vibrational motion of the nuclei. For a single Gaussian function, a large negative value of the exponential parameter would result in a highly localized, steep function of r_1, meaning there is little variance in the internuclear distance. A diffuse Gaussian in the coordinate r_1 would point to increased vibrational activity and a nonrigid nuclear framework, conditions where the Born–Oppenheimer approximation can fail. Of course, for a trial function made up of many basis functions, the analysis of the interplay between parameters and molecular properties becomes more complex. Nonetheless, the spectrum of values for m_k used in this calculation, and in our calculations on the isotopomers of the hydrogen molecule, provide us with a useful benchmark when constructing trial functions for other diatomic systems.

TABLE II. The time for completion of the first energy and gradient calculation(as calculated by the MPI routine DTIME), expressed as the ratio of the time for n processors to the time for 8 processors. Representative wave functions were used for the calculations.

n	8-term	24-term	64-term	128-term	512-term
1	7.63	7.83	7.73	8.41	7.33
2	3.92	3.88	4.14	3.82	3.70
4	1.99	1.94	2.09	1.89	1.87
8	1.00	1.00	1.00	1.00	1.00

TABLE III. Expectation values for the LiH nonadiabatic ground state using symmetry projected, explicitly correlated Gaussian wave functions with from 8 to 512 basis functions. Energy is given in hartrees, and distance in bohrs.

	8	24	48	64	128	256	512
$\langle H \rangle$	−7.966 776 013 5	−8.037 869 791 4	−8.056 391 690 0	−8.059 247 743 7	−8.063 649 853 5	−8.065 563 369 5	−8.066 155 763 8
$\langle T \rangle$	7.966 775 977 0	8.037 869 726 8	8.056 390 034 8	8.059 247 746 4	8.063 649 519 9	8.065 575 796 8	8.066 192 936 8
$\langle V \rangle$	−15.933 551 991	−16.075 739 518	−16.112 781 725	−16.118 495 490	−16.127 299 373	−16.131 139 166	−16.132 348 701
η	1.000 000 002 3	1.000 000 004 0	1.000 000 102 7	0.999 999 999 8	1.000 000 020 7	0.999 999 229 6	0.999 997 695 8
$\|g\|_2^2$	2.441×10^{-13}	6.418×10^{-14}	1.137×10^{-9}	1.174×10^{-13}	7.919×10^{-11}	9.879×10^{-8}	4.406×10^{-8}
$\langle r_1 \rangle$	3.125 213 547 3	3.080 094 879 2	3.081 349 410 7	3.075 715 392 2	3.066 234 224 7	3.062 140 992 7	3.061 065 098 5
$\langle r_1^2 \rangle$	9.807 943 368 3	9.528 067 494 5	9.536 746 012 1	9.503 584 920 3	9.445 639 268 3	9.424 997 868 6	9.417 964 494 4

A. Timing results

As mentioned before, the code we used was parallelized using MPI and run on a four node cluster of dual processor Linux workstations. Since the symmetry projector for the ket $(\mathcal{P}^\dagger \mathcal{P})$ contains 24 terms, this allowed for a ''division of labor'' among the 8 processors when calculating matrix elements of symmetry projected functions. Each processor in our cluster calculated 3 of the 24 integrals required for each matrix element. Table II displays timing data for optimization runs on 1, 2, 4, and 8 processors for trial functions ranging in size from 8-term to 512-term. The value of the nonlinear parameters were randomly generated in MATLAB, and the same set of parameters used in all runs for both series of calculations. The time given in Table II is the time for completion of the first energy and gradient call made during optimization, normalized to the time for execution on 8 processors. The time for completion of the first energy and gradient call is that reported by the MPI routine DTIME. Inspection of the table shows the effectiveness of parallelization, the time on 1 processor being approximately eight times that of the time on 8 processors. For larger wave functions parallelization becomes critical to fully optimize the wave functions in a reasonable amount of time.

B. Energy results

Table III gives expectation values for the nonadiabatic ground state of LiH from optimized wave functions consisting of between 8 and 512 basis functions. Included in the table 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 $\langle r_1 \rangle$ and $\langle r_1^2 \rangle$.

The rapid convergence of this basis set and high degree of optimization of the wave functions is evidenced by inspection of the table. This is no doubt partially attributable to the efficient integral and analytic gradient formulas used in the calculations, as well as the improvement in representing the nuclear motion introduced by inclusion of the premultipliers.

Since our work represents the first non-Born–Oppenheimer calculations on LiH direct comparison of our results is not possible. Instead we have taken the Born–Oppenheimer LiH ground state energy of −8.070 553 hartree reported by Cencek and Rychlewski[8] and added a zero-point energy of 0.003 098 hartree, which is one half the value of $\Delta G_{1/2}$ taken from the experimental result cited in the work

of Partridge and Langhoff.[9] This gives an estimated lower-bound non-Born–Oppenheimer energy of −8.067 455 hartree. The energy result of −8.066 155 763 8 hartree presented in this work could no doubt be improved upon by using a larger basis set. The only obstacle to performing higher accuracy calculations with larger basis sets is the availability of computational resources. Based on our previous calculations on the H_2 isotopomers, where the lowest ever ground state energies were obtained with 512 Gaussians, we realize that it would require a significantly larger basis set to achieve similar accuracy for LiH. Future generations of massively parallel computers may provide enough computer power to run such calculations on LiH and on even larger systems.

VII. FUTURE DIRECTIONS

We believe explicitly correlated Gaussians with the r_{ij}^m premultipliers show great promise for use in nonadiabatic variational computations of high accuracy. Such calculations are particularly important for lighter diatomics in demonstrating the effects of the Born–Oppenheimer approximation. Our calculations on LiH are the first such calculations on a diatomic system with more than two electrons. The principle obstacle in studying systems with more electrons is the daunting task of computing matrix elements of symmetry projected trial functions, since the number of elements in the Young projection operator scales as the factorial of the number of electrons. Fortunately the speed and efficiency of optimization can be greatly improved by running calculations on a ''Beowulf'' cluster. The algorithms used in evaluating symmetry projected matrix elements lend themselves naturally for use on such parallel clusters. We hope to expand our 8-processor cluster in the near future, making possible accurate calculations on systems with more electrons.

We are planning to develop a more general basis set of the form $\phi_k = \Pi_{i<j} r_{ij}^{m_{k,ij}} \exp[-\mathbf{r}'(\mathbf{L_k L_k'} \otimes \mathbf{I_3})\mathbf{r}]$, that could be employed in calculations on molecular systems with more than two nuclei. In addition we will extend this basis to include higher angular momentum states. This development will allow us to describe nonadiabatic states of a general N-body system.

ACKNOWLEDGMENTS

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