Nonadiabatic Calculations of the Dipole Moments of LiH and LiD

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We present very high-accuracy fully nonadiabatic calculated values for the dipole moments for the ground states of LiH and LiD. These results were calculated via numerical differentiation of the energy obtained at different electric field strengths. The values for the energy were obtained from variational optimization with analytical gradients of the wave function expanded in a basis of explicitly correlated floating *s*-type Gaussian functions. The values obtained for LiH and LiD, 2.3140 and 2.3088 a.u., are nearly identical to those obtained by experiment.

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Very-high-accuracy dipole moments are some of the most difficult molecular properties to calculate via the conventional electronic structure methods in use today. This difficulty is due to the Born-Oppenheimer (BO) approximation. The dipole moment is inherently a function of the instantaneous correlated motions of the electrons and nuclei, and the artificial separation of these motions involved in the BO approximation reduces the accuracy of the calculated values for systems containing light nuclei. In BO calculations, one determines the fictitious electronic dipole and then uses the potential energy surface for the system to calculate corrections due to nuclear motion (molecular vibration). It has been shown [1] that even relatively simple, stable molecules can have non-negligible corrections to purely electronic properties, suggesting that these contributions should not be neglected.

There have been several recent attempts to find the nuclear corrections to the LiH dipole moment. Papadopoulos *et al.* [2] used the perturbation theory to calculate the corrections, and Tachikawa and Osamura [3] used the dynamic extended molecular orbital method to try to calculate the nonadiabatic result directly. Results for these methods are reported in Table I. In all cases, the calculated values are outside of the range of the experimental results [4,5], also reported in Table I.

In this work we present a method for calculating the dipole moment directly using a variational non–Born-Oppenheimer wave function expanded in a basis set of floating, *s*-type explicitly correlated Gaussian (FSECG) basis functions. This basis has been used for calculations invoking the BO approximation (see [6] and the references cited therein, also [7]). This work represents the first application of this basis to non-BO calculations.

The FSECG basis is excellent for calculating nonadiabatic molecular properties due to the flexibility of the functions. The functional "centers" describing the average nuclear and electronic positions can move in three-dimensional space, allowing for the effect of a perturbation, such as an electric field, on the molecular wave function to be accurately described. Basis functions used in previous non-BO calculations [8–11] may not have this flexibility. The calculations of non-BO molecular properties in the FSECG basis may be the most comparable to experiment, as the least amount of approximations have to be made in the theory (i.e., no BO approximation, no orbital approximation, etc.).

In the equations below, capital letters represent matrices, lowercase letters represent vectors, and lowercase Greek letters represent scalars. Any exceptions to this scheme should be obvious and are pointed out.

A system of $n + 1$ particles (six for LiH) can be transformed to a system with three coordinates describing the motion of the center of mass and $3n$ coordinates describing the internal motion of a system of n pseudoparticles. The positions in the laboratory coordinate frame of the original six particles in LiH, i.e., Li nucleus, H nucleus, and the four electrons, may be collected in a vector of length 18, made by stacking the 3-vectors, R_i containing the xyz coordinates of the six particles:

$$R = \begin{pmatrix} R_1 \\ R_2 \\ \vdots \\ R_6 \end{pmatrix}.$$

TABLE I. Experimental (expt.) and theoretical (calc.) dipole moments (μ) for LiH and LiD from the literature. All the values are in atomic units. The values given in parentheses are experimental uncertainty.

	μ
LiH	
[2], calc.	2.317
[3], calc.	2.389
[4], expt.	2.3145
[5], expt.	2.314(0.001)
LiD	
[3], calc.	2.392
[5], expt.	2.309(0.001)

A transformation matrix, T,

$$T = \begin{pmatrix} \frac{M_1}{M_T} & \frac{M_2}{M_T} & \frac{M_3}{M_T} & \frac{M_4}{M_T} & \frac{M_5}{M_T} & \frac{M_6}{M_T} \\ -1 & 1 & 0 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \otimes I_3$$

(M_i is the mass of the ith particle and M_T is the sum of all these masses, $\otimes$ denotes a Kronecker product, and I_3 is the 3×3 identity matrix) takes the R vector into a set of coordinates in the internal coordinate frame for the center of mass and the five pseudoparticles:

$$TR = r_0 + r\,,$$

where r_0 is a 3-vector of the coordinates of the center of mass of the system stacked on top of a vector of length 15 containing the internal coordinates of the remaining five particles:

$$r = \begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_5 \end{pmatrix}.$$

We will refer to the mass of the particle at the origin of the internal coordinate system as M_0 and to the reduced masses of the n pseudoparticles as m_i. The charges of the original particles (Q_i) map directly to the corresponding pseudoparticles (q_{i-1}), with the charge of the particle at the origin of the internal coordinate system mapping to a central potential ($Q_1 \rightarrow q_0$).

We use the non-Born-Oppenheimer nonrelativistic internal Hamiltonian with the semiclassical particle/static electric field interaction term:

$$\hat{H} = -\frac{1}{2}\left(\sum_{i}^{5} \frac{1}{m_i}\nabla_i^2 + \sum_{i \neq j}^{5} \frac{1}{M_0}\nabla_i'\nabla_j\right) + \sum_{i=1}^{5} \frac{q_0 q_i}{r_i} + \sum_{i<j}^{5} \frac{q_i q_j}{r_{ij}} - \mu \cdot \varepsilon\,, \qquad (1)$$

where μ is the dipole moment vector and ε is the electric field vector.

The dipole interaction operator above references only the internal coordinate system, or the *pseudoparticles*. This is because in a neutral system the operator in the laboratory coordinate system transforms to an operator for the internal coordinate system plus a term for the center of mass that is identically zero. The operator for LiH in the laboratory coordinate frame can be written as

$$\mu \cdot \varepsilon = (\varepsilon_6)' Q \otimes I_3 R\,,$$

where ε_6 is a vector of length 18 which is the normal ε vector stacked on top of itself six times and Q is a 6×6 matrix with the charge Q_i on the i, ith diagonal, and zeros elsewhere. We can substitute $T^{-1}(r_0 + r)$ for R in the above operator and obtain

$$\mu \cdot \varepsilon = (\varepsilon_6)'(QT^{-1}) \otimes I_3(r_0 + r)\,.$$

When this operator is expanded, we obtain a term for the electric field interacting with the sum of the charges of all the particles located at the center of mass:

$$\varepsilon \cdot r_0 \sum_{i=1}^{6} Q_{ii} = \varepsilon \cdot r_0 \sum_{i=0}^{5} q_i\,,$$

which obviously sums to zero for a neutral system, indicating that the center of mass of a neutral system does not accelerate in an electric field. We also obtain terms for the five pseudoparticles

$$\mu \cdot \varepsilon = \sum_{i=1}^{5} \varepsilon \cdot r_i q_i\,,$$

which is how we formally define the interaction term.

The FSECG basis function for n pseudoparticles is

$$g_k(r) = \exp[-(r - s_k)' A_k \otimes I_3 (r - s_k)]\,, \qquad (2)$$

where s_k is a $3n$-vector of "shifts" which are variational parameters and A_k is a symmetric $n \times n$ matrix of variational exponential parameters.

The square integrability of the basis can be assured by writing A_k in Cholesky factored form as

$$A_k = L_k L_k'\,, \qquad (3)$$

where L_k is a lower triangular matrix whose elements can vary in the range $[-\infty, \infty]$. The basis functions may then be written as

$$g_k(r) = \exp\{-(r - s_k)'[(L_k L_k') \otimes I_3](r - s_k)\}\,. \qquad (4)$$

For each subset of identical pseudoparticles i, we can implement the desired permutational symmetry into the basis functions by projection onto the irreducible representation of the permutation group, S_{n_i}, for total spin S_i using the appropriate projection operator $\hat{E}_i$. The total projection operator would then be a product:

$$\hat{E} = \prod_i \hat{E}_i\,. \qquad (5)$$

For fermions, the projection operators are simply Young operators, derived from the appropriate Young tableau, as shown in the previous work [6].

Thus the final form of the basis function is

$$\hat{E} g_k(r) = \prod_i \hat{E}_i \exp\{-(r - s_k)'[(L_k L_k') \otimes I_3] \times (r - s_k)\}\,, \qquad (6)$$

and the spin-free spatial wave function has the form

$$\Psi = \sum_{k=1}^{m} c_k \hat{E} g_k\,, \qquad (7)$$

where m is the size of the basis.

We calculate the dipole moment from total energy values for the ground state of LiH/LiD in different electric field strengths. The energy values are obtained as variationally optimized expectation values of the Hamiltonian operator defined above:

$$E = \min \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi \mid \Psi \rangle}. \tag{8}$$

The wave function (7) is optimized with respect to the parameters L_k, s_k, and c_k. This leads to $\frac{1}{2}n(n + 1) + 3n + 1$ variational parameters (31 for LiH) per basis function. We begin with an initial guess for the wave function and then use analytical gradients in a truncated Newton-type algorithm to find the lowest value for the energy. The ith component of the dipole moment is calculated numerically from the definition:

$$\mu_i = \frac{\partial E}{\partial \varepsilon_i}. \tag{9}$$

The energy was calculated for each basis with three electric field strengths, $\varepsilon_z = 0$, -0.0016, and -0.0032 a.u., and the energy curve was fitted with a second order polynomial in ε_i. μ is then the first order coefficient of this fit. In the fully non-BO approach, applying electric fields in different directions is meaningless since the wave function has spherical symmetry and will have the same dipole moment in any direction. Thus while we formally say that we calculate the ith component of the dipole moment, we really calculate only one value, the observable dipole moment. The integrals and gradients needed to solve (8) and (9) are similar to those presented in [6], and will be presented explicitly in a future paper.

Optimization was carried out by supplying the function and energy gradients to the optimization routine TN [12], which was downloaded from the World Wide Web [13]. The program was coded in parallel using MPI, and was executed on several different platforms: a Beowulf cluster [14] of 8 dual processor PII and PIII machines with 400 and 500 MHz processors and 512 MB of RAM per machine; an SGI Origin 2000 with 104 400 MHz R12K processors and 48 GB of RAM; and a cluster of 16 Sun Ultra 10's with 400 MHz processors and 256 MB of RAM per machine. The program scales well with the number of processors in the range of 1–32 processors, and comprehensive timing results will be presented in a future paper.

The 244 term non-BO wave functions were variationally optimized for LiH and LiD. The initial guess for the LiH non-BO wave function was built by multiplying a 244 term BO wave function expanded in a basis of explicitly correlated functions by Gaussians for the H nucleus centered at and around (in all three dimensions) a point separated from the origin by the equilibrium distance of 3.015 bohrs along the direction of the electric field. Thus the centers corresponding to the hydrogen nucleus were scattered from about 2.9 to about 3.1 bohrs. The lithium nucleus was, of course, placed at the origin of the internal coordinate system. The functional centers corresponding to the electrons were located primarily on the two nuclei, with two electrons at the origin (about 0.0 ± 0.001 bohrs in all three directions) and two electrons near the H nucleus (about 3.05 ± 0.06 bohrs) per basis set. This reflects the strong ionic character in the lithium/hydrogen bond. The LiD non-BO wave function was optimized starting from the converged LiH wave function. Wave functions of various smaller expansion lengths were optimized for LiH alone. Table II shows the convergence properties of the dipole moment for these basis sets. It can be seen that the calculated value of the dipole converges and reaches a value near that of experiment, 2.314 a.u., as larger basis sets are used. The reported results for all functions were converged to the point where the squared norm of the total gradient was at least of the order 10^{-8} and the energy changed at most in the ninth decimal place. At this point the dipole moment was converged to seven decimal places, which is more than experimental accuracy. The total variational energy (also in Table II) for our 244 term wave function is $-8.063\,633\,1$ hartree. The most accurate non-BO energy calculated before was that of Scheu *et al.* [11] equal to $-8.066\,155\,7$ hartree. Thus our energy value for this basis set is in error by only about 0.0025 hartree. Despite this small error, we deem the obtained convergence of the dipole moment value with the basis set size quite satisfactory and it is highly unlikely that further enlargement of the basis can change this value by an amount close to the uncertainty level of the experiment where the LiH/LiD dipole moments were measured.

The optimized basis functions show strong correlation between the nuclei, the nuclei and the electrons, and between the electrons. The centers describing the H/D nucleus show a spread of values from about 2.9 bohrs to 3.1 bohrs, with the expectation value for the inter-nuclear distance being 3.063 bohrs for LiH and 3.052 bohrs for LiD. These values are in good agreement with the value 3.061 bohrs for LiH obtained by Scheu *et al.* [11] in their non-BO calculations, and are, as expected, longer than the BO "equilibrium" value. Our values are believed to be much more accurate than those of [3],

TABLE II. Values for energies, virial coefficients (η), and dipole moments (μ), for non-BO LiH/D for various expansion lengths (m). All values are in atomic units.

m	$\langle H \rangle$	η	μ
LiH			
24	$-8.042\,329\,4$	1.000 000	2.4047
64	$-8.059\,298\,8$	1.000 000	2.3394
104	$-8.061\,926\,7$	1.000 000	2.3261
144	$-8.062\,932\,4$	0.999 999	2.3149
244	$-8.063\,633\,1$	0.999 999	2.3140
Experimental			2.314 ± 0.001 [5]
LiD			
244	$-8.065\,033\,1$	1.000 000	2.3088
Experimental			2.309 ± 0.001 [5]

which are 3.119 937 and 3.104 819 bohrs for LiH and LiD, respectively.

The value of the dipole moment of LiH obtained in this work, 2.3140 a.u., is essentially identical to the experimental value, 2.314 ± 0.001 [5]. Our calculations simulate experiment more closely than any previous calculations. The results also provide validation of the perturbation approach of [2], since the perturbation result, 2.317 a.u., is very close to our value. At the same time, our results are much more accurate than those of [3], the only other "direct" calculation of the LiH dipole moment. The value of the dipole moment of LiD, 2.3088, is also of good accuracy, compared to the experimental result, 2.309 ± 0.001 [5]. Again, our result is much more accurate than that of [3].

There are a few issues which must be discussed when comparing the values obtained with our method to experimental values. When an electric field is turned on, the Hamiltonian no longer commutes with the $\hat{J}^2$ operator, but does commute with the $\hat{J}_z$ operator. Thus our wave function must be an eigenfunction of $\hat{H}$ and $\hat{J}_z$ but not $\hat{J}^2$ (except in the zero field case). The basis functions we use are not rigorously eigenfunctions of $\hat{J}_z$, but the optimization of the wave function makes them very close to the state with $M_J = 0$. The experimental results are obtained for the ground electronic and vibrational states with $J = 1$. The change in the dipole moment in going from the $J = 0$ state that we simulated in the calculations to the $J = 1$ state that was observed experimentally should be very small and we do not expect it to affect the comparison presented in this work.

We mentioned that our value for average position of the H nucleus is less than 0.002 bohr larger than that obtained by Scheu *et al.* Going to a larger basis set we would reach a slightly lower lithium/hydrogen distance which in turn would lower the dipole moment somewhat. Based on the convergence of the dipole moment value with the basis set size obtained in the calculations, we have a reason to believe that this change should be quite small and again should not affect the reported values. Going to a larger basis at this time would be quite expensive as we must optimize wave functions in four field strengths per basis.

In conclusion, we presented the first direct nonadiabatic variational calculations of dipole moments in a basis of floating explicitly correlated Gaussians. The results obtained are of experimental quality. The basis introduced here for non-BO calculations may be an excellent one for calculations of molecular properties in general.

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