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Application of a Force Constraint to an Approximate Wavefunction of LiH

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A total electrostatic force constraint is imposed on a ten-term lithium hydride wavefunction at each of three values of the internuclear distance. Both the equilibrium internuclear separation and the quadratic force constant are found to improve significantly.

Für eine aus zehn Termen bestehende Wellenfunktion für Lithiumhydrid wurde bei drei Werten des Kernabstandes der gesamte Einfluß durch elektrostatische Kräfte miteinbezogen. Sowohl der Wert für den Gleichgewichtsabstand der Kerne als auch für die quadratische Kraftkonstante wurden deutlich verbessert.

Une contrainte électrostatique totale est imposée à une fonction d'onde à 10 termes de l'hydrure de lithium pour trois valeurs de la distance internucléaire. La séparation internucléaire d'équilibre et la constante de force quadratique en sont notablement améliorées.

1. Introduction

The relationship between calculations based on the Born-Oppenheimer approximation and spectroscopic parameters (such as the quadratic force constant k_e and the equilibrium internuclear separation R_e) for a diatomic molecule has been a subject of considerable interest[1]. Recently, a variety of constraints has been formulated [4] for the explicit purpose of improving force constant calculations. The purpose of the present work is to test one of them with a numerical example.

2. Calculations

The system chosen for this investigation is the ground state of lithium hydride. We place the LiH molecule on the z-axis with $z(\mathrm{H}) - z(\mathrm{Li}) = R$. First, we obtained a free-variational wavefunction. It is a ten-term valence-bond configuration-interaction function built from 18 Slater-type atomic orbitals. The basis orbitals, together with their exponents, are given in Table 1; and the valence-bond terms are listed in Table 2. The orbital exponents have been systematically, though not completely, optimized. A parabolic fit of the energies at $R = 2.75$, 3.00, and 3.25 a_0 gives a minimum of -8.022299 hartrees at $R = 3.0826\ a_0$. Our free variational result is not as good as some of the more extensive calculations on LiH [6–11], but is better than many of the other computations[2].

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[1] See, for example, Refs. [1–3].

[2] In addition to the compendia [12–14], see also Refs. [3, 15, 16].

Table 1. *Atomic orbitals and exponents at various internuclear distances R*

Designation[a]	Orbital	Orbital exponents		
		$R=2.75a_0$	$R=3.00a_0$	$R=3.25a_0$
01	$1s$ (Li)	3.2796	3.2807	3.2823
02	$1s'$ (Li)	2.0799	2.0814	2.0838
21	$2s$ (Li)	0.7150	0.7264	0.7201
22	$2s'$ (Li)	0.7492	0.7271	0.7184
23	$2s''$ (Li)	0.8370	0.7294	0.6716
24	$2s'''$ (Li)	0.5937	0.6384	0.6508
61	$2p_0$ (Li)	0.8949	0.9036	0.7957
62	$2p'_0$ (Li)	0.6991	0.6749	0.6548
63	$2p''_0$ (Li)	0.7861	0.7590	0.7226
11	$1s$ (H)	1.1805	1.3564	1.2452
12	$1s'$ (H)	1.0337	0.9589	0.9961
13	$1s''$ (H)	1.3561	1.2988	1.3048
14	$1s'''$ (H)	0.6855	0.6789	0.6707
31	$2s$ (H)	1.6277	1.3315	1.4462
32	$2s'$ (H)	1.7119	1.6635	1.6311
51	$2p_{-1}$ (H)	1.2227	1.2346	1.1892
71	$2p_0$ (H)	0.4425	0.4181	0.4388
91	$2p_{+1}$ (H)	1.2227	1.2346	1.1892

[a] Texas designation: the last digit is like a subscript; the other digits are identical to those used in Ref. [5].

Table 2. *Valence-bond configurations used*

j	ϕ_j
1	(01, 02; 21, 11)[a]
2	(01, 02; 61, 12)
3	(01, 02; 22, 31)
4	(01, 02; 13, 14)
5	(01, 02; 51, 91)
6	(01, 02; 62, 32)
7	(01, 02; 63, 71)
8	(01, 02; 23, 24)
9	(01, 02; 13, 31)
10	(01, 02; 13, 71)

[a] $(a, b; c, d) = |a\alpha, b\beta, c\alpha, d\beta| + |a\alpha, b\beta, d\alpha, c\beta| + |b\alpha, a\beta, c\alpha, d\beta| + |b\alpha, a\beta, d\alpha, c\beta|$.

The constraint tested in this work is zero total electrostatic force on the nuclei:

$$C(R) = F_{\mathrm{Li}}(R) + F_{\mathrm{H}}(R) = 0\,, \tag{1}$$

where F_A is the z-component of the electrostatic force on nucleus A. The formulation and the solution of the equations for constrained variation are straightforward [4, 17].

The results for both constrained and free variational calculations at three values of R are summarized in Table 3. These results show three interesting features: 1) The sacrifice in energy caused by the force constraint is about 0.06 hartree, a reasonable price to pay for the removal of a total electrostatic

Table 3. *Summary of results of constrained variational calculation. Free-variational results are given in parentheses. Atomic units are used*

R	2.75	3.00	3.25
E	-7.962886	-7.964854	-7.962572
	(-8.018264)	(-8.022050)	(-8.021277)
F_{Li}	-0.028	-0.018	-0.030
	(0.134)	(0.150)	(0.160)
F_{H}	0.028	0.018	0.030
	(0.057)	(0.032)	(0.016)
μ[a]	-0.3578	-0.0922	$+0.3010$
	(-2.1432)	(-2.2278)	(-2.3250)

[a] Dipole moment.

Table 4. *Properties based on a parabolic fit of the results in Table 3. Atomic units are used*

	Free	Constrained	Experimental
E_e	-8.022299	-7.964857	-8.0703[a]
R_e	3.0826	2.9908	3.015[b]
k_e	0.07294	0.06800	0.06591[b]
μ_e	-2.2585	-0.1043	-2.3143[c]
$\lvert d\mu/dR\rvert_{R_e}$	0.380	1.299	0.29 ± 0.03[d]

[a] Ref. [18]. — [b] Ref. [19].

[c] Ref. [20]. This is not μ at R_e but is a vibrationally averaged value.

[d] Ref. [21].

force of about $0.18\, e^2 a_0^{-2}$ on the nuclei. 2) Although the total electrostatic force is removed by the constraint, the components F_{Li} and F_{H} remain repulsive even at $R \geq R_e$. 3) The electric dipole moment μ shows a drastic change from free variation to constrained variation.

The results listed in Table 3 are now interpolated by a parabolic fit. The equilibrium internuclear distance R_e is defined by $(dE/dR)_{R_e} = 0$. Various properties evaluated at R_e are presented in Table 4. Comparison of the free variational results with the experimental values shows that the overall quality of ψ is reasonable for a ten-term wavefunction. The results of the force constraint is more striking. On one hand, there are a small sacrifice of energy and a large cost in the accuracy of the dipole moment and dipole derivative. On the other hand, both R_e and the quadratic force constant k_e have improved considerably. The error has been reduced from 2.2% to 0.8% for R_e and from 10.7% to 3.2% for k_e.

3. Discussion

It is clear from our results that electrostatic forces calculated from approximate wavefunctions do not represent the true forces operating in a molecule. In order to understand why the force constraint can possibly work, we regard $C(R)$ in Eq. (1) from another point of view. In terms of the set of fixed electron coordinates f

[2, 4], $C(R)=0$ simply means that $\langle\psi|(\partial H/\partial R)_f|\psi\rangle$ should be independent of the origin of the space-fixed axes. In other words, Eq. (1) is a legitimate theoretical constraint even without the connotation of electrostatic forces. In this work, we have discovered that such a constraint somehow improves the calculations of R_e and k_e. Whether this is a general phenomenon or not remains to be tested with other numerical examples. Since getting the free-variational eigenvectors requires the most effort and computer time, we hope that other workers will be encouraged by our results to test the force constraint on the wavefunctions they already have or are getting.

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