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A Scaled United Atom Model for Diatomic Hydrides

By

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An eigenfunction for a diatomic hydride is approximated by a scaled eigenfunction (or linear combination of scaled eigenfunctions) for the corresponding united atom or separated ion (e.g., LiH, Be and Li^-, respectively). All "atomic" contributions to the resulting energy expressions are obtained exactly from experiment. The sum of one-electron two-center coulomb interactions between the scaled united atom or separated ion charge density and proton are approximated by integrals over orthogonalized Slater atomic orbitals. Configuration interaction is invoked in three cases. Force constants, equilibrium internuclear distances and electronic excitation energies are computed and compared with available experimental data.

Eigenfunktionen für zweiatomige Hydride werden durch Eigenfunktionen mit Skalenfaktor (oder Linearkombinationen von diesen) des entsprechenden vereinigten Atoms oder getrennten Ions (z. B. LiH, Be bzw. Li^-) approximiert. Alle atomaren Beiträge zu den resultierenden Energieausdrücken erhält man exakt vom Experiment. Die Summe der Wechselwirkungen zwischen Elektronen (beschrieben durch Funktionen des vereinigten Atoms bzw. getrennten Ions) und Proton wird durch Integrale über orthogonale Slaterfunktionen approximiert. Konfigurationswechselwirkung wird in drei Fällen zugezogen. Kraftkonstanten, Gleichgewichtsabstände der Kerne und Elektronenanregungsenergien werden berechnet und mit den verfügbaren experimentellen Daten verglichen.

La fonction propre d'un hydrure diatomique est approximée par une fonction scalée (ou une combinaison lináire de telles fontcions) pour l'atome unifié ou l'ion séparé (p. ex.: LiH, Be et Li^-, respectivement). Toutes les contributions «atomiques» aux eneries résultantes s'obtiennent exactement de l'expérience. Les interaction de Coulomb monoélectroniques dicentriques entre l'atome unifié scalé ou l'ion séparé et le proton sont approximées par d'intégrales sur des orbitales orthogonalisées de Slater. L'interaction de configurations est appelée en trois cas. On calcule les constantes de force, les distances internucléaires d'équilibre et les compare aux données expérimentales.

Introduction

One rather simple model for predicting internuclear distances and force constants for hydrides was suggested some time ago by Platt [*14*], studied critically by Clinton [*2*] and by Bratoz, Daudel, Roux and Allavena [*1*], modified by Hall and Rees [*7*], and applied to diatomic hydride ions by Moran and Friedman [*12*]. In the Hall-Rees modification, the total electron density for a diatomic hydride is taken from an atomic calculation, either the united atom (with nuclear charge $Z + 1$) or the separated ion (with nuclear charge Z). This electron density is assumed to be spherically symmetrical and it is modified for each internuclear distance by a scale factor determined by energy optimization.

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There are three objectives of the work reported here: 1. to remove the assumption of a spherically symmetrical electron density; 2. to test the applicability of the model for predicting excitation energies; and 3. to extend the model by including configuration interaction.

Theory

The electronic hamiltonian operator written in atomic units for an N-electron diatomic hydride MH might be written

$$\mathcal{H} = T + ZA + B + C\,, \tag{1}$$

where

$$T = -\tfrac{1}{2}\sum_i^N \nabla_i^2 \tag{2}$$

$$A = -\sum_i^N \frac{1}{r_{\mathrm{M}i}} \tag{3}$$

$$B = -\sum_i^N \frac{1}{r_{\mathrm{H}i}} \tag{4}$$

$$C = \sum_i^N \sum_{j>i}^N \frac{1}{r_{ij}}\ ; \tag{5}$$

Z is the atomic number of nucleus M. The Hamiltonian for the united atom corresponding to an internuclear distance $R = 0$ is

$$\mathcal{H}_U = T + (Z+1)\,A + C\ ; \tag{6}$$

for the separated ion resulting if a proton is removed from MH, the hamiltonian is

$$\mathcal{H}_I = T + ZA + C\,. \tag{7}$$

Therefore,

$$\mathcal{H} = \mathcal{H}_U - A + B \tag{8}$$

$$= \mathcal{H}_I + B\,. \tag{9}$$

We consider next the use of scaled eigenfunctions of $\mathcal{H}_U$ or $\mathcal{H}_I$ as variational trial functions for the diatomic system MH.

Let $\Psi\,(r_i \ldots r_N)$ be a normalized eigenfunction of $\mathcal{H}_U$ or $\mathcal{H}_I$. If each electron coordinate r_i in Ψ is replaced by sr_i, where s is a scaling parameter, and then if the resulting function is renormalized, we obtain the normalized scaled eigenfunction

$$\Psi_s = s^{3N/2}\,\Psi\,(sr_l \ldots sr_N)\,. \tag{10}$$

In the united atom case, we may write [4]

$$E = E_U\, s\,(2-s) - sL_U/(Z+1) + s\bar{B}\,, \tag{11}$$

where $E_U = \int \Psi^* \mathcal{H}_U \Psi d\tau$ and $L_U = (Z+1)\int \Psi^* A \Psi d\tau$ are the exact total electronic energy and nuclear attraction energy, respectively, of the real united atom, and $\bar{B} = \int \Psi^* B \Psi d\tau$ is a function of $\varrho = sR$. In the separated ion case,

$$E = E_I\, s\,(2-s) + s\bar{B}\,. \tag{12}$$

The total diatomic molecular energy for fixed nuclei is given by $\mathcal{E} = E + Z/R$, where Z/R is the nuclear repulsion energy. The optimum value of s for each internuclear distance R is determined by energy minimization.

Table. *Calculated and Experimental Properties of Diatomic Hydrides*

Molecular State	Atomic States	$T_e \times 10^{-3}$ cm^{-1}	ω_e cm^{-1}	$k \times 10^{-5}$ dyne cm^{-1}	r_e bohrs
H_2 $X^1\Sigma_g^+$	$1s^2\ {}^1S_g$	0	4089	4.97	1.40
			3862	4.43	1.46
			4395	5.71	1.40
HeH $X^2\Sigma^+$	$2s\ {}^2S_g$	0	917	0.40	2.28
			196	0.02	3.17
LiH $X^1\Sigma^+$	$2s^2\ {}^1S_g$	0	1163	0.70	3.38
			657	0.23	4.89
			1406	1.03	3.02
BeH $X^2\Sigma^+$	$2p\ {}^2P_u$	0	2245	2.69	2.62
			1615	1.39	3.26
			2059	2.26	2.54
BeH $A^2\Pi$	$2p\ {}^2P_u$	23.3	1540	1.27	3.00
		18.8	1108	0.66	3.73
		20.0	2088	2.33	2.52
BH $X^1\Sigma^+$	$2p^2\ {}^1D_g$	0	3694	7.43	2.09
	$2p^2\ {}^1S_g$		2962	4.78	2.42
			2367	3.05	2.34
BH $a^3\Pi$	$2p^2\ {}^3P_g$	16.5	2822	4.33	2.30
		19.4	2255	2.77	2.67
					[2.27]
BH $A^1\Pi$	$2p^2\ {}^1D_g$	26.3	2822	4.33	2.30
		24.0	2255	2.77	2.67
		23.1	2345	2.99	2.31
BH $b^3\Sigma^-$	$2p^2\ {}^3P_g$	41.3	1841	1.85	2.69
		40.8	1468	1.17	3.13
					[2.31]
BH $^1\Delta$	$2p^2\ {}^1D_g$	51.1	1841	1.85	2.69
		45.4	1468	1.17	3.13
BH $B^1\Sigma^+$	$2p^2\ {}^1D_g$	59.1	1877	1.92	2.68
	$2p^2\ {}^1S_g$	48.8	1478	1.19	3.13
		(52.3)	(2400)	(3.13)	2.30
CH $X^2\Pi$	$2p^3\ {}^2D_u$	0	4475	10.98	1.86
	$2p^3\ {}^2P_u$		3802	7.92	2.08
			(2862)	4.49	2.12
CH $^4\Sigma^-$	$2p^3\ {}^4S_u$	8.6	3295	5.95	2.07
		14.8	2789	4.26	2.32
CH $A^2\Delta$	$2p^3\ {}^2D_u$	27.3	3295	5.95	2.07
		26.1	2789	4.26	2.32
		(23.2)	2921	4.67	2.08

Table (Continued)

Molecular State	Atomic States	$T_e \times 10^{-3}$ cm^{-1}	ω_e cm^{-1}	$k \times 10^{-5}$ dyne cm^{-1}	r_e bohrs
CH $B^2\Sigma^+$	$2p^3\,{}^2D_u$	27.3	3295	5.95	2.07
		26.1	2789	4.26	2.32
		(25.9)	2543	3.54	2.24
CH $C^2\Sigma^+$	$2p^3\,{}^2P_u$	36.7	3292	5.94	2.08
		30.9	2789	4.26	2.32
		(31.8)	2824	4.36	2.10
CH ${}^2\Pi$	$2p^3\,{}^2D_u$	57.4	2136	2.50	2.46
	$2p^3\,{}^2P_u$	51.0	1780	1.74	2.75
NH $X^3\Sigma^-$	$2p^4\,{}^3P_g$	0	5134	14.6	1.69
			4507	11.3	1.85
			(3300)	(6.03)	1.96
NH $a^1\Delta$	$2p^4\,{}^1D_g$	$a' = 15.6$	5134	14.6	1.69
		$a'' = 10.5$	4501	11.3	1.85
		a	[3186]		[1.97]
NH $b^1\Sigma^+$	$2p^4\,{}^1D_g$	$a' + 10.7$	5060	14.2	1.69
	$2p^4\,{}^1S_g$	$a'' + 7.5$	4474	1.11	1.85
		$a + (8.5)$	(3480)	(6.7)	1.98
NH $A^3\Pi$	$2p^4\,{}^3P_g$	32.5	3641	7.35	1.91
		27.9	3199	5.67	2.09
		(29.8)	(3300)	(6.03)	1.96
NH $c^1\Pi$	$2p^4\,{}^1D_g$	$a' + 32.5$	3641	7.35	1.91
		$a'' + 29.9$	3199	5.67	2.09
		$a + (31.3)$	[2119]		[2.13]
NH $d^1\Sigma^+$	$2p^4\,{}^1D_g$	$a' + 64.4$	2511	3.49	2.25
	$2p^4\,{}^1S_g$	$a'' + 57.0$	2125	2.50	2.48
		$a + (70.5)$	(2640)	(3.86)	[2.13]
OH $X^2\Pi$	$2p^5\,{}^2P_u$	0	5633	17.73	1.57
			5070	14.35	1.69
			3735	7.79	1.83
OH $A^2\Sigma^+$	$2p^5\,{}^2P_u$	32.4	3886	8.44	1.79
		30.2	3494	6.82	1.92
		32.7	3181	5.65	1.91
HF $X^1\Sigma^+$	$2p^6\,{}^1S_g$	0	5988	20.2	1.48
			5485	17.0	1.57
			4139	9.67	1.73

For ground states of the united atoms and separated ions, non-relativistic values of E_U, L_U and E_I obtained from empirical atomic data are used directly in this work [5, 15]. For excited states of the same systems, experimental (hence, relativistic) excitation energies (or, for negative ions, excitation energies extrapolated from experimental isoelectronic series) are utilized; the average nuclearelectron attraction energy L_U is assumed to be identical for all electronic states of the same electron configuration (e.g., ^3P_g, ^1D_g and ^1S_g, $1s^2 2s^2 2p^2$). Finally, $\overline{B}$ is computed using the appropriate united atom or separated ion wave functions built from orthogonalized Slater atomic orbitals [*13*], however, using $Z_{\text{eff}}\,(1s) = Z - 0.3125$.

In line with all previous work, the above description is directed toward prediction of the equilibrium internuclear distance R_e and force constant k for the lowest energy electronic state of any given symmetry (which would include, of course, the ground electronic state). If one is interested also in a state not the lowest of a given symmetry, then configuration interaction must be invoked. In principle, this will yield an improved description of the lowest state, as well as a prediction of the excitation energy T_e.

In such configuration interaction treatments, the matrix element

$$H_{nm} = \int \psi^*_{ns} \mathscr{H} \psi_{ms} \, d\tau \tag{13}$$

is required; here, ψ_{ns} and ψ_{ms} are scaled eigenfunctions for the nth and mth atomic states, both normalized and both containing the common scale factor s. For each internuclear distance R, optimum values of the scale factor s for each diatomic state are obtained by independently minimizing each energy root of the secular determinant [*16*]. Using Eq. (1) we may write

$$H_{nm} = \int \psi^*_{ns} \left[T + ZA + C\right] \psi_{ms} \, d\tau + \int \psi^*_{ns} B \psi_{ms} \, d\tau \tag{14}$$

where $T + ZA + C$ is the hamiltonian operator for a mononuclear species with nuclear charge Z and N electrons. If the atomic functions ψ_{ns} and ψ_{ms} have different eigenvalues of the operator L^2 (square of total orbital angular momentum), then the first integral in Eq. (14) will vanish. If we consider those diatomic states which correlate with atomic eigenstates associated with the lowest electron configuration only, then this simplification applies in all cases treated here. The final integral in Eq. (14) is computed in the same manner as $\overline{B}$ in Eqs. (11) or (12); viz., using united atom or separated ion wave functions built from orthogonalized Slater atomic orbitals [*13*].

Results

In the table, we list complete results for the first-row diatomic hydrides. We indicate in the second column the atomic eigenfunctions used in the approximation. For example, the $X^2\Sigma^+$ and $A^2\Pi$ states of BeH are approximated by scaled $1s^2\, 2s^2\, 2p\ ^2P$ eigenfunctions of boron ($M_L = 0$ and $+\ 1$ components, respectively) in the united atom model or similar states of Be^- in the separated ion model. Configuration interaction is invoked in approximating the $^1\Sigma^+$ states of BH and NH and the $^2\Pi$ states of CH.

For each diatomic state, the first line contains results of the united atom approximation and the second line results of the separated ion treatment; experimental results when available are given in the third line using HERZBERG's notation [*8*].

For completeness, we list both the fundamental vibrational frequency ω_e as well as the force constant $k = (\partial^2 \mathscr{E}/\partial R^2)_e$ in spite of the fact that they are related. The error in the former always appears less than in the latter since $\omega_e \propto k^{\frac{1}{2}}$

It can be seen that the model performs rather well in predicting fundamental vibrational frequencis and equilibrium internuclear distances. Furthermore, the average absolute error in the united atom model predictions of term values T_e is only 3.36×10^3 cm^{-1}; in the separated ion model, it is 2.72×10^3 cm^{-1}.

For the lowest triplet state of BH, the united atom model gives $T_e = 16500$ cm^{-1}. This is to be compared with previous predictions of 8113 cm^{-1} and 8956 cm^{-1} by Ellison [*6*] and Hurley [*9*], respectively. It seems rather clear that the value given by the present model is too high here. For the lowest quartet excited state of CH, we obtain $T_e = 8600$ cm^{-1}; again, there have been previous predictions of 3640 cm^{-1} [*3*], 4840 cm^{-1} [*9*] and 3230 cm^{-1} [*11*]. A semiempirical model proposed by P. C. H. Jordon and H. C. Longuet-Higgins [*10*] gives 13970 cm^{-1} for this state; however, their model yields term values for the observed $^2\Delta$, $^2\Sigma^-$ and $^2\Sigma^+$ states which are 6700 to 9600 cm^{-1} too high. Finally, the united atom term value for the lowest singlet state of NH is 15600 cm^{-1}, which agrees well with Hurley,s prediction 14200 cm^{-1} [*9*].

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