

Energy Expectation Values and the Integral Hellmann–Feynman Theorem: H_2^+ Molecule

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It is by now well known that the integral Hellmann–Feynman (IHF) theorem has little quantitative utility for chemically interesting problems, although the formalism potentially affords a ready physical interpretation of changes in molecular conformation. In this paper, the IHF theorem is applied to variational and simple LCAO wavefunctions for the H_2^+ ground state, which range in quality from crude to essentially exact. The IHF results improve quite dramatically with the quality of the wavefunctions. This suggests that errors in the IHF formula may be of the same order as those in the wavefunction. (In contrast, errors in variationally determined energies are of second order.) Our results suggest a convenient test which can be applied to any revised IHF formalism developed in the future.

I. INTRODUCTION

The energy change $E_Y - E_X$ in any isoelectronic process $X \rightarrow Y$ is predicted by the integral Hellmann–Feynman (IHF) theorem, which since its development has been applied principally to the internal-rotation problem.^{1–5} The success of the theorem in such chemically interesting applications has unfortunately been rather unimpressive. Efforts to improve or modify the formalism are accordingly in progress in this and other laboratories.⁶

The IHF theorem holds exactly for exact wavefunctions. Obviously, however, only approximate wavefunctions, usually of the variational type, are available in nontrivial applications. The success of the theorem is therefore directly related to the quality of the approximate wavefunctions. Until now, there has been no systematic investigation of the IHF theorem applied to wavefunctions of widely varying quality—ranging from crude to essentially exact. Since we believe such detailed understanding to be essential to correct application of the IHF theorem, or to any modification thereof, we have undertaken such a series of computations on the hydrogen molecule-ion, perhaps the simplest system of chemical interest which can be so treated.

The two-parameter Guillemin–Zener wavefunctions are simple yet exceedingly accurate. Using variational parameters determined by Hirschfelder,⁷ these functions yield energies which agree with the exact values to within 5×10^{-4} a.u. for the full range of internuclear separations. Hence, the IHF theorem can, for the first time, be applied to a molecule for which essentially exact wavefunctions are known and for which the effects of electron correlation are not present.

In addition, the slightly less accurate one-parameter Guillemin–Zener functions and two other wavefunctions of lesser quality, the Finkelstein–Horowitz and the Pauling (LCAO) functions,⁷ have been applied to the IHF theorem. Some results based on the least accurate of these, the LCAO functions, have already been reported.⁶

II. IHF FORMALISM

Consider the isoelectronic process $R \rightarrow R'$ in H_2^+ : stretching the internuclear distance from R to R' . The associated electronic Schrödinger equations for the molecule are

$$[\mathfrak{I}'(\mu', \nu') + V'(\mu', \nu')] \psi_{R'}(\mu', \nu') = E_{R'} \psi_{R'}(\mu', \nu'), \quad (1a)$$

$$[\mathfrak{I}(\mu, \nu) + V(\mu, \nu)] \psi_R(\mu, \nu) = E_R \psi_R(\mu, \nu). \quad (1b)$$

The variables μ', ν', μ, ν represent confocal ellipsoid coordinates: $\mu' = (r_a' + r_b')/R'$, $\nu' = (r_a' - r_b')/R'$, $\mu = (r_a + r_b)/R$, and $\nu = (r_a - r_b)/R$; r_a' and r_b' are the distances from the electron to the nuclei a' and b' (separated by R'), while r_a and r_b are the corresponding distances to nuclei a and b . Now let (1a) be multiplied by $\psi_R^*(\mu, \nu)$ and (1b) by $\psi_{R'}^*(\mu', \nu')$. Integrate each equation over all space and subtract the second equation from the first. This yields

$$\begin{aligned} \Delta E_{\text{IHF}} &= E_{R'} - E_R \\ &= S'^{-1} \int d\tau' \psi_R^*(\mu, \nu) V'(\mu', \nu') \psi_{R'}(\mu', \nu') \\ &\quad - S^{-1} \int d\tau \psi_{R'}^*(\mu', \nu') V(\mu, \nu) \psi_R(\mu, \nu). \end{aligned} \quad (2)$$

The following identities have been employed:

$$\begin{aligned} \mathfrak{I}(\mu, \nu) &= -2[R^2(\mu^2 - \nu^2)]^{-1} \\ &\quad \times \left\{ \frac{\partial}{\partial \mu} (\mu^2 - 1) \frac{\partial}{\partial \mu} + \frac{\partial}{\partial \nu} (1 - \nu^2) \frac{\partial}{\partial \nu} \right\}, \\ V(\mu, \nu) &= -4\mu[R(\mu^2 - \nu^2)]^{-1}, \end{aligned} \quad (3a)$$

$$\int d\tau \dots = 2\pi \left(\frac{R}{2}\right)^3 \int_1^\infty d\mu \int_{-1}^1 d\nu (\mu^2 - \nu^2) \dots,$$

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² R. E. Wyatt and R. G. Parr, *J. Chem. Phys.* **44**, 1529 (1966).

³ W. H. Fink and L. C. Allen, *J. Chem. Phys.* **46**, 3270 (1967).

⁴ M. P. Melrose and R. G. Parr, *Theoret. Chim. Acta* **8**, 150 (1967).

⁵ S. M. Rothstein and S. M. Blinder, *Theoret. Chim. Acta* **8**, 427 (1967), and Refs. 2–7 therein.

⁶ S. T. Epstein, A. C. Hurley, R. E. Wyatt, and R. G. Parr, *J. Chem. Phys.* **47**, 1275 (1967).

⁷ S. Kim, T. Y. Chang, and J. O. Hirschfelder, *J. Chem. Phys.* **43**, 1092 (1965).

and

$$S = \int d\tau \psi_R^*(\mu, \nu) \psi_R(\mu', \nu'). \quad (3b)$$

Corresponding relations for \mathcal{J}' , V' , $\int d\tau'$, and S' are the obvious analogs.

Let two additional quantities ΔT and ΔS be defined:

$$\Delta T \equiv S'^{-1} \int d\tau' \psi_R^*(\mu, \nu) \mathcal{J}'(\mu', \nu') \psi_R(\mu', \nu') - S^{-1} \int d\tau \psi_R^*(\mu', \nu') \mathcal{J}(\mu, \nu) \psi_R(\mu, \nu), \quad (4a)$$

$$\Delta S \equiv S' - S. \quad (4b)$$

It is evident that these must both equal zero.⁸ The quantities (ΔS and ΔT) are actually very useful since their calculated values provide a check on the reliability of the numerical quadrature. In particular, as ΔT becomes large with respect to zero, values of ΔE_{IHF} , calculated using (2), should become inaccurate. Obviously, the utility of ΔT and ΔS is an artifact of the coordinate system; in spherical polar coordinates originating from the midpoint of the two protons, ΔS and ΔT would be trivially zero.⁹

It should be noted that the IHF formula (2) is formally equivalent to

$$\Delta E_{\text{IHF}} = \int d\tau \psi_R^* \Delta \mathcal{H} \psi_R, \quad (5)$$

where $\Delta \mathcal{H} \equiv V' - V$. Equation (2) is used since it has computational advantages over (5).

III. NUMERICAL RESULTS

The IHF formula (2) has been applied to the Guillemin-Zener, Finkelstein-Horowitz, and Pauling functions. The reader is referred to Ref. 7 for a detailed discussion of these wavefunctions.

All integrations are carried out numerically on a IBM 7090 computer. The μ (or μ') integrals were mapped into the ranges (0, 1) and (2, ∞).¹⁰ The integrals over the first range were approximated by a 32-point Gaussian quadrature, those over the second range by a 32-point Gaussian-Laguerre quadrature. Similarly, a 32-point

Gaussian-Legendre quadrature over the range (0, 1) was used for the ν (or ν') integrals. The resulting IHF values are compiled in Table I; each entry required about 30 sec of computer time.

The results reported here are probably reliable to four significant figures since they changed only by a few units in the fourth place when the μ integrals were mapped into the range (0, ∞) and evaluated by a 32-point Gaussian-Laguerre quadrature, the ν integrals being calculated as before. Finally, the largest values of ΔT and ΔS were less than 10^{-4} a.u., indicating that the numerical integrations were reasonably reliable.

IV. DISCUSSION

The most striking feature of these computations is the dramatic improvement of the IHF values with increasing quality of the wavefunction. In particular, when R is small and the molecule is stretched just a few atomic units, the Finkelstein-Horowitz energy-expectation-value differences deviate just 1% or 2% from the corresponding exact values. The corresponding IHF results are, however, in error by 20%-30%. The IHF results for the Guillemin-Zener functions are, by contrast, in error by only a few percent. Finally, the IHF results derived from the LCAO functions are very poor, reflecting the crude nature of these functions, particularly for small values of R .

The numerical results show that ΔE_{IHF} has invariably more than twice the error of ΔE_{SUB} . The latter is, by virtue of the variational principle, of second order. It is strongly suggested, therefore, that the IHF theorem produces (at least) a *first-order* error in ΔE , which appears to support the analysis given by Musher.¹²

The IHF results for larger values of R (3 or 4 a.u.) are consistent with the trends exhibited by the difference of the energy expectation values. In particular, the Guillemin-Zener results have a small error while the Finkelstein-Horowitz and LCAO results have about the same, much larger error. This is to be expected since the exponential parameter of the Finkelstein function approaches unity, its value for the LCAO function. The latter two functions are very nearly equivalent energetically for large R , and the IHF results are correspondingly close.

The LCAO results call for some additional comment. They are in error by some 50% throughout the entire range of R values despite the improvement of the functions for larger R , as indicated by the difference of expectation values. This is to some extent numerical since the energy differences at small R are larger than those at larger R where relative errors are magnified. Nevertheless, the IHF results do not improve as rapidly as they should as R becomes larger. All this illustrates

⁸ ΔT contains the volume integral $\int d\tau (\psi_R \nabla^2 \psi_R - \psi_R \nabla^2 \psi_R)$. By Green's theorem, this can be transformed to a surface integral $\int (\psi_R \nabla \psi_R \cdot d\mathbf{\sigma} - \psi_R \nabla \psi_R \cdot d\mathbf{\sigma})$. As the integration is extended over all space, there do indeed arise nonvanishing contributions from surface elements enclosing the nuclei, owing to the cusps in ψ , hence, discontinuities in $\nabla \psi$. However, since ψ and $\nabla \psi$ are both finite at the nuclei, these contributions, and hence ΔT , approach zero in the limit as the surface elements about the nuclei are collapsed to points. See also J. O. Hirschfelder and G. V. Nazarov, J. Chem. Phys. **34**, 1666 (1961).

⁹ S.M.R. acknowledges a conversation with Prof. R. M. Pitzer on this and a closely related subject.

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¹¹ D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. (London) **A246**, 215 (1953).

¹² J. I. Musher, J. Chem. Phys. **43**, 2145 (1965).

TABLE I. Integral Hellmann-Feynman energy differences in H_2^+ for variational and simple LCAO wavefunctions.^{a-c}

R	R'	ΔE^d	Two-parameter Guillemin-Zener		One-parameter Guillemin-Zener		Finkelstein and Horowitz		Pauling (LCAO)		
			ΔE_{IHF}^e	ΔE_{SUB}^f	ΔE_{IHF}^e	ΔE_{SUB}^f	ΔE_{IHF}^e	ΔE_{SUB}^f	ΔE_{IHF}^e	ΔE_{IHF}^g	ΔE_{SUB}^f
1.0	2.0	0.3492	0.3523(0.9)	0.3491	0.3538(1.3)	0.3490	0.2663(24)	0.3545(2)	0.1568(56)		0.2346(33)
1.0	3.0	0.5409	0.5397(0.0)	0.5408	0.5384(0.0)	0.5407	0.4194(22)	0.5432(0)	0.2407(55)		0.3960(27)
1.0	4.0	0.6557	0.6462(1.4)	0.6556	0.6415(2.2)	0.6556	0.5196(21)	0.6537(0)	0.2761(58)		0.5015(24)
1.0	5.0	0.7274	0.7069(2.8)	0.7273	0.6993(3.9)	0.7274	0.5849(20)	0.7218(1)	0.2863(61)		0.5692(22)
1.0	8.0	0.8242	0.7688(6.7)	0.8241	0.7616(7.6)	0.8240	0.6718(18)	0.8143(1)	0.2660(60)		0.6616(20)
2.0	3.0	0.1917	0.1946(1.5)	0.1917	0.1942(1.3)	0.1917	0.1236(36)	0.1887(2)	0.1029(46)	0.1096(43)	0.1614(16)
2.0	4.0	0.3066	0.3074(0.0)	0.3066	0.3046(0.7)	0.3067	0.2024(34)	0.2992(2)	0.1556(49)	0.1938(37)	0.2669(13)
2.0	5.0	0.3782	0.3727(1.5)	0.3783	0.3674(2.9)	0.3785	0.2537(33)	0.3673(3)	0.1794(53)	0.2675(29)	0.3346(12)
2.0	8.0	0.4751	0.4404(7.3)	0.4750	0.4345(8.6)	0.4750	0.3173(33)	0.4598(3)	0.1870(61)		0.4270(10)
3.0	4.0	0.1148	0.1183(3.0)	0.1149	0.1175(2.4)	0.1150	0.0657(44)	0.1104(3)	0.0615(48)	0.0657(43)	0.1056(8)
3.0	5.0	0.1865	0.1891(1.4)	0.1866	0.1867(0.0)	0.1868	0.1081(42)	0.1786(4)	0.0938(50)	0.1180(37)	0.1732(7)
3.0	6.0	0.2323	0.2297(1.1)	0.2324	0.2261(2.7)	0.2325	0.1346(42)	0.2220(4)	0.1100(53)		0.2167(7)
3.0	8.0	0.2833	0.2654(6.3)	0.2833	0.2630(7.2)	0.2833	0.1601(44)	0.2710(4)	0.1206(57)		0.2657(6)
4.0	5.0	0.0717	0.0758(5.7)	0.0717	0.0753(5.0)	0.0718	0.0374(48)	0.0681(5)	0.0362(50)	0.0389(46)	0.0677(6)
4.0	8.0	0.1685	0.1623(3.7)	0.1684	0.1632(3.1)	0.1684	0.0841(50)	0.1606(5)	0.0744(56)		0.1601(5)
4.0	10.0		0.1785	0.1954	0.1824	0.1952	0.0930	0.1870	0.0803		0.1866

^a All numbers in atomic units.^b Energy differences are the electronic energy for internuclear distance R' less than that at R for H_2^+ ground state.^c Numbers in parenthesis are percent error relative to exact values.^d Exact values; Ref. 11.^e Integral Hellmann-Feynman formula; Eq. (2) of text. Both ends of the molecule are displaced an equal distance until they are separated by R' atomic units.^f Difference of the energy expectation values; Ref. 7.^g Values for keeping one atom stationary and displacing the other until they are separated by R' atomic units; Ref. 6.

that the IHF theorem is useless for very approximate wavefunctions—by now, a well-known shortcoming.¹²

The previously reported IHF results for the LCAO functions⁶ are consistently larger than our values. We should, however, like to emphasize that the same program which generates the very accurate Guillemin-Zener IHF values also generates the LCAO results reported here, which gives us confidence in our numbers. Finally, the two calculations are not entirely equivalent. In Ref. 6, one atom is kept stationary as the molecule is stretched. In contrast, we displace both atoms symmetrically. Consequently, the respective ΔH operators are not the same. Lowe and Mazziotti¹³ have recently shown that the former IHF path for H_2^+ is optimal.¹⁴ For exact wavefunctions, the results would become equal, of course.

¹³ J. P. Lowe and A. Mazziotti, *J. Chem. Phys.* **48**, 877 (1968).

¹⁴ Further analysis to be published (S.M.R.).

To summarize, IHF computations are very sensitive to the accuracy of the wavefunction, exhibiting evidently an error at least of the same order as that in the wavefunction. Any future modification of the IHF formalism, to be quantitatively successful, must remove this sensitivity. The H_2^+ molecule might provide a good test for such revised theory since there are available wavefunctions which are simple, yet essentially exact.

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Scattering of Velocity-Filtered Atomic Beams of Ar and Xe from the (111) Plane of Silver*

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The scattering of nearly monoenergetic atomic beams of Ar and Xe from the (111) plane of silver has been studied as a function of the nominal velocity v_0 transmitted by a slotted-disk velocity selector (SDVS) used as a velocity filter on the incident thermal-energy (Maxwellian) beam. The selector has a velocity spread of $\pm 0.19 v_0$ and studies were carried out over a range of v_0 from 2.2×10^4 to 5.3×10^4 cm/sec. The scattered beam distributions were found to be directed, corresponding closely to those of Maxwellian beams when $v_0 = \bar{v} = \frac{3}{2}(2\pi k T_B/M)^{1/2}$, the average velocity of the corresponding Maxwellian beam of temperature T_B . These results, together with the results of earlier scattering studies, imply that the thermal motion of the lattice is the dominant factor in producing the spatial dispersion as well as the velocity dispersion in the scattered beam that has been observed by other investigators. The most likely origin of these dispersive effects is the languidness of the collision in the sense used by Goodman to describe gas atom-lattice collisions.

I. INTRODUCTION

In most studies of directed scattering of molecular beams from solid surfaces, ideal specular scattering is rarely observed. Even though the maximum scattered intensity may lie at the specular angle, the dispersion of the scattered beam is much broader than that of the incident beam. In fact, it has been found that the probability $P(\theta_r)$ for finding the scattered beam at the reflected angle θ_r is a function of many variables.¹ The variables that have been observed experimentally to be relevant include the incident angle, the beam energy, the surface temperature, the solid and gas masses, and the heat of adsorption. Additionally, in most molecular beam-surface scattering experiments, beams (originat-

ing from Knudsen sources) that have a Maxwellian distribution of velocities have been used. It is natural, therefore, to assume the existence of a conditional probability $P(\theta_r | v_i)$ for scattering at θ_r for each incident velocity v_i . The observed dispersion of the scattered beam could then result in part from the averaging of $P(\theta_r | v_i)$ over the Maxwellian distribution of v_i in the incident beam and might tend, therefore, to obscure the details of the scattering phenomena. This type of velocity averaging has been proposed previously by several authors.^{2,3}

Aerodynamic nozzle-beam sources can yield considerably higher translational energies (~ 1.0 eV) than are available with Knudsen sources (< 0.5 eV) but only at the expense of fluid enthalpy, and hence the resulting

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¹ For ideal specular scattering $P(\theta_r) = 1$ if $\theta_r = \theta_i$ and 0 otherwise. For diffuse scattering, $P(\theta_r) \propto \cos \theta_r$, only, but we shall restrict this discussion to directed scattering.

² J. N. Smith, Jr., *J. Chem. Phys.* **40**, 2520 (1964).

³ J. J. Hinchey and E. S. Malloy, *Fundamentals of Gas Surface Interactions*, H. Saltsburg, J. N. Smith, Jr., and M. Rogers, Eds. (Academic Press Inc., New York, 1967), p. 448.