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ABSTRACT

The perturbation theory of the constrained variational method is applied to a calculation on the lithium hydride molecule by Browne and Matsen[7]. The changes in various properties on constraining the expectation values of force and virial operators to vanish are calculated. It is shown that the perturbation series converge very rapidly, so that only the leading terms are required. However, in this particular case the imposition of the constraints has a negligible effect on the calculated properties.

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INTRODUCTION

It is well known that if the error in a variationally determined wave function is of order Δ , then whereas the energy is correct to order Δ^2, the error in the expectation values of other operators (except constants of motion) is of order Δ . An interesting approach introduced by Mukherji and Karplus[1] and developed recently by Whitman and his collaborators[2,3] is to constrain the variational wave function to give the known theoretical or experimental value μ for the expectation value $\langle \mathcal{M} \rangle$ of some operator $\mathcal{M}$. This constraint will cost a certain amount of energy ΔE, but if the difference $\Delta\mu$ between μ and the free variational value of $\langle \mathcal{M} \rangle$ is small, then ΔE will only be of order $\Delta\mu^2$. On the other hand, the expectation value $\langle \mathcal{L} \rangle$ of another operator $\mathcal{L}$ of interest will change by an amount ΔL of order $\Delta\mu$ in general.

If the approximate variational wave function is a fairly good one, so that $\Delta\mu$ is indeed small, a perturbation approach is indicated, and has been formulated by one of us[4] in a paper which will be referred to as I . This approach leads to expressions for ΔE and ΔL as power series in $\Delta\mu$, which may hopefully be approximated adequately by the leading terms, or truncated after the first few terms. The extension of the theory to the imposition of more than one constraint is also

given in I .

The results of applying constraints to calculations on hydrogen fluoride[1], lithium hydride[2] and helium[3] have been encouraging. In paper I the perturbation approach was tested on the lithium hydride calculation of Robinson[5], which was used by Rasiel and Whitman. It was found that the perturbation series did not converge very rapidly in this case. The lithium hydride constraint calculations have been repeated recently[6] using an improved technique in the direct calculation and extending the perturbation calculation. It was concluded that the perturbation approach is to be recommended for constraining variational treatments employing large basis sets.

The object of the present paper is to apply the perturbation theory of constraints to an accurate variational calculation by Browne and Matsen[7] on the ground state of the lithium hydride molecule using a 28-term wave function.

THEORY

The theory upon which the constraint calculations are based has been given in paper I . The basic equations for the changes ΔE and ΔL due to the constraint $\langle(\mathcal{H}-\mu)\rangle = 0$ are

$$\Delta E = \sum_{n=1}^{\infty} \lambda^n E^{(n)}, \tag{1}$$

$$\Delta L = \sum_{n=1}^{\infty} \lambda^n E^{(1,n)}, \tag{2}$$

where λ is an auxiliary parameter given by the smallest root of

$$\Delta\mu = \sum_{n=2}^{\infty} n\lambda^{n-1} E^{(n)}, \tag{3}$$

where

$$\Delta\mu = \langle(\mu - \mathcal{M})\rangle_{free} \tag{4}$$

is the deviation of the expectation value of $\mathcal{M}$ in the unconstrained treatment from the theoretical value μ. The coefficients $E^{(n)}$ in Eqs. (2) and (3) are the perturbation energies for the perturbation of the Hamiltonian $\mathcal{H}$ of the system by the operator $(\mathcal{M}-\mu)$, calculated within the basis of eigenfunctions of the free variational approximation. The coefficients $E^{(1,n)}$ are similarly the energies for the double perturbation of $\mathcal{H}$ by the operators $\mathcal{L}$ and $\mathcal{M}-\mu$ respectively[8].

If two constraints

$$\langle \mathcal{M}_1 \rangle = \mu_1 \quad \text{and} \quad \langle \mathcal{M}_2 \rangle = \mu_2 \tag{5}$$

are imposed, the corresponding equations are

$$\Delta E = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda_1^n \lambda_2^m E^{(n,m)} - E^{(0,0)}, \tag{6}$$

$$\Delta L = \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \lambda_1^n \lambda_2^m E^{(1,n,m)} - E^{(1,0,0)}, \tag{7}$$

where λ_1 and λ_2 are the smallest roots of the simultaneous constraint equations

$$\Delta\mu_1 \equiv \langle (\mu_1 - \mathcal{M}_1) \rangle_{free} = \sum_{n=2}^{\infty} \sum_{m=0}^{\infty} n \lambda_1^{n-1} \lambda_2^m E^{(n,m)}, \tag{8}$$

$$\Delta\mu_2 \equiv \langle (\mu_2 - \mathcal{M}_2) \rangle_{free} = \sum_{n=0}^{\infty} \sum_{m=2}^{\infty} m \lambda_1^n \lambda_2^{m-1} E^{(n,m)}. \tag{9}$$

The double perturbation energies $E^{(n,m)}$ are for the perturbation operators $(\mathcal{M}_1 - \mu_1)$ and $(\mathcal{M}_2 - \mu_2)$, and $E^{(1,n,m)}$ are triple perturbation energies for operators $\mathcal{L}$, $(\mathcal{M}_1 - \mu_1)$ and $(\mathcal{M}_2 - \mu_2)$ respectively.

UNCONSTRAINED TREATMENT

The treatment of lithium hydride to which the foregoing theory has been applied is described in the paper[7] by Browne and Matsen, to which we refer for full details. The variational wave function was a linear combination of 28 terms[9] with $^1\Sigma^+$ symmetry, each term being built from four orbitals chosen from a mixed set of Slater-type and simple elliptic orbitals. The 28 coefficients at the calculated equilibrium distance were computed for us by Professor F. A. Matsen and Mr. C. E. Rodriquez of the University of Texas, and are given in the appendix.

The results of the free variational treatment are very good. The calculated equilibrium distance, energy and dipole moment are 3.046 Bohrs - 8.055841 Hartrees and 5.889 Debyes, compared with the experimental values 3.013, -8.0703 and 5.882. However, the expectation value of the total force on the nuclei is not zero but 0.014 a.u., and as the wave function was not scaled the virial theorem is not exactly satisfied. It is therefore of interest to see what changes result from imposing constraints on the force and virial operators, although the changes may be expected to be small.

CONSTRAINTS

Three independent theoretical constraints were considered, based on the Hellmann-Feynman and virial theorems. According to the former the expectation values of the force operators, $\mathcal{F}_L$ and $\mathcal{F}_H$, for the nuclei of LiH should vanish in the equilibrium configuration. These operators may be defined by (atomic units)

$$\mathcal{F}_L = -3/R^2 + 3\sum_{j=1}^{4} \cos\theta_{jL}/r_{jL}^2 , \tag{10}$$

$$\mathcal{F}_H = 3/R^2 + \sum_{j=1}^{4} \cos\theta_{jH}/r_{jH}^2 , \tag{11}$$

where force is positive in the direction Li $\rightarrow$ H, θ_{jL} is the angle jLH and θ_{jH} is the supplement of $\angle$jHL. The expectation value of the total force

$$\mathcal{F} = \mathcal{F}_L + \mathcal{F}_H \tag{12}$$

should vanish for all configurations. The expectation value of the operator

$$\mathcal{V} = \mathcal{H} + \mathcal{T} , \tag{13}$$

where $\mathcal{K}$ is the kinetic energy operator, should vanish for the equilibrium configuration according to the virial theorem. Note that if the free variational wave function was scaled, then $\langle \mathcal{V} \rangle$ would vanish automatically.

In this work the single constraints $\mathcal{F}$, $\mathcal{F}_L$, $\mathcal{F}_H$ and $\mathcal{V}$ and the four pairs of double constraints $(\mathcal{F}_L, \mathcal{F}_H)$, $(\mathcal{F}_L, \mathcal{V})$, $(\mathcal{F}_H, \mathcal{V})$ and $(\mathcal{F}, \mathcal{V})$ were applied. In all cases the theoretical values of the μ's are zero.

CONSTRAINED CALCULATIONS

In order to evaluate the perturbation coefficients $E^{(n)}$, $E^{(l,n)}$, $E^{(l,n,m)}$ it is necessary to know all the 28 eigenfunctions and eigenvalues of the secular equations associated with the freely varied trial wavefunction. These unconstrained basis eigenfunctions and eigenvalues had not been obtained at the calculated equilibrium distance, and were computed for us by Professor F. A. Matsen and Mr. C. E. Rodriquez. The matrix elements of the constraint and property operators in the unconstrained basis, which occur in the expressions for $E^{(n)}$, etc., given in paper I, were also computed for us by Dr. J. C. Browne and Mr. C. E. Rodriquez.

Considerable attention was paid to the convergence of the perturbation series for ΔE, ΔL, etc. However, in all cases the simple leading approximations presented in paper I were entirely adequate. This can be seen from the following detailed results for

two cases.

Single Constraint: Total Force

If $\mathcal{H} = \mathcal{F}$, the total force operator, the perturbation energy coefficients $E^{(1)}$ to $E^{(5)}$ (Hartrees) are 0.0143258, -17.3975, -0.849213, -0.0149703, 0.167555. By inverting Eq. (3) to give λ in powers of $\Delta\mu$ one gets

$$\lambda = 4.11721 \times 10^{-4} - 1.24 \times 10^{-8} - 1.20 \times 10^{-9} - 2.5 \times 10^{-13} + O(\Delta^5),$$

$$= 4.11708 \times 10^{-4} .$$

The first term is thus sufficient. When λ is substituted into Eq. (1) it becomes

$$\Delta E = 5.8980 \times 10^{-6} - 2.9489 \times 10^{-6} - 5.93 \times 10^{-11}$$
$$-4.30 \times 10^{-12} + 1.98 \times 10^{-16} + O(\lambda^6)$$
$$= 2.949 \times 10^{-6} \text{ Hartrees}$$

The leading approximation, consisting of the first two terms[10], is therefore sufficient. The series (2) also converges rapidly. For example, when $\mathcal{L}$ is the dipole moment operator,

$$\Delta L = -1.2097 \times 10^{-3} + 9.96 \times 10^{-7} + 1.08 \times 10^{-9} + O(\lambda^4)$$
$$= -1.2087 \times 10^{-3} \text{ a.u.}$$

Double Constraint: Force and Virial

When $\mathcal{H}_1 = \mathcal{F}$ and $\mathcal{H}_2 = \mathcal{V}$, Eq. (6) for the cost in energy of the double constraint is

$$\Delta E = 5.8899 \times 10^{-6} + 4.373 \times 10^{-7}$$
$$-2.9408 \times 10^{-6} - 4.48 \times 10^{-9} - 2.154 \times 10^{-7}$$
$$-5.90 \times 10^{-11} - 1.82 \times 10^{-9} + 8.91 \times 10^{-12} - 7.03 \times 10^{-11}$$
$$+ 0 (\lambda^4)$$
$$= 3.1646 \times 10^{-6} \text{ Hartrees}$$

Here again, the leading approximation[11] is sufficient. The convergence of the series (7) may be illustrated for $\mathcal{L} = \mathcal{F}_L$, the force on the Li nucleus:

$$\Delta F_L = -1.41610 \times 10^{-2} + 2.79 \times 10^{-5}$$
$$-6.64 \times 10^{-7} - 8.79 \times 10^{-6} + 1.30 \times 10^{-8} + 0(\lambda^3)$$
$$= -1.4142 \times 10^{-2} \text{ a.u.}$$

If the force F_H on the proton is also calculated through terms of order λ^2, although F_H and F_L are of order 10^{-4}, the sum $F_H + F_L$ is of order 10^{-12}, thus checking that the imposed constraint $\langle \mathcal{F} \rangle = 0$ has been satisfied.

RESULTS

The results for the various single and double constraints are summarized in Tables I and II. It can be seen that the sacrifice in energy is practically negligible in all cases, of order 10^{-6} Hartrees or less. On the other hand, although the constraints undoubtedly improve the wave function slightly,

the effect on the calculated dipole moment is almost negligible. This is not surprising, since the unconstrained value is already so close to the experimental. However, it does indicate that the calculated value is stable.

It is interesting to observe that the force and virial constraints are practically independent. $\langle \mathcal{V} \rangle$ does not change when $\mathcal{M} = \mathcal{F}$, and $\langle \mathcal{F} \rangle$ does not change when $\mathcal{M} = \mathcal{V}$. Among the single constraints, that of the total force appears to be slightly superior, and leads to a dipole moment nearer the experimental value[12]. Among the double constraints, the pair $\mathcal{F}$ and $\mathcal{V}$ appear to be most satisfactory.

In Table III the unconstrained and constrained values of various properties are listed for the single constraint $\mathcal{M} = \mathcal{F}$ and the double constraint $\mathcal{M}_1 = \mathcal{F}$ and $\mathcal{M}_2 = \mathcal{V}$. The properties are essentially the expectation values of r^2, r^{-1}, $r^2 P_2(\cos\theta)$ and $r^{-3} P_2(\cos\theta)$ for one or both nuclei[13]. We have presented them in the form of the following physical properties (defined in terms of atomic units):

a) Diamagnetic contribution to susceptibility at nucleus A,

$$\chi(A)^d = -\frac{1}{6}\alpha^2 \left\langle \sum_{j=1}^{4} r_{jA}^2 \right\rangle ,$$

where α is the fine structure constant ($\cong 1/137$).

b) Diamagnetic contribution to shielding constant of nucleus A,

$$\sigma(A)^d = \tfrac{1}{3}\alpha^2 \left\langle \sum_{j=1}^{4} r_{jA}^{-1} \right\rangle .$$

c) Electrical quadrupole moment with respect to centre of mass C,

$$Q_{zz} = 3R_{LC}^2 + R_{HC}^2 + \left\langle \sum_{j=1}^{4} r_{jC}^2 P_2(\cos\theta_{jC}) \right\rangle ,$$

where $\theta_{jC} = \angle$ jCH .

d) Electric field gradient at Li nucleus,

$$q(Li) = 2R^{-3} - 2\left\langle \sum_{j=1}^{4} r_{jL}^{-3} P_2(\cos\theta_{jL}) \right\rangle .$$

It is somewhat surprising to find that the constrained values do not differ significantly from the free variational values for any of the properties listed. The stability of the expectation values to different kinds of constraints suggests that they are indeed rather accurate.

CONCLUSION

The main conclusion to be drawn from this paper is that the effect of theoretical constraints on good approximate wave functions can be calculated rather easily from the leading terms of a perturbation treatment. The quantities required for the calculation can be readily obtained by a slight extension of the main computer programme.

The other conclusion is that since the Browne and Matsen[7] wave function for LiH is almost immune to improvement by two different types of constraint, it must be rather good.

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APPENDIX

The wave function used by Browne and Matsen[7] in their variational calculation of the ground state of LiH has the form

$$\Psi = \sum_{j=1}^{28} c_j \Psi_j$$

where the Ψ_j are 4-electron terms with $^1\Sigma$ symmetry. Browne and Matsen quoted the ground state coefficients c_j for R = 3.0 Bohr, but not for the interpolated equilibrium separation R_e(calc.) = 3.046. The coefficients at the calculated R_e have been computed by Matsen and Rodriquez, and are given in Table A. The numbering is identical to that in Table II, p. A1229 of reference 7, so that the term designation has not been repeated. The orbital exponents were the same as those given in Table IV of reference 7, for R = 3.0 .

REFERENCES

1. A. Mukherji and M. J. Karplus, J. Chem. Phys., 38, 44 (1963).
2. Y. Rasiel and D. R. Whitman, J. Chem. Phys., 42, 2124 (1965).
3. D. R. Whitman and R. Carpenter, Bull. Am. Phys. Soc., 9, 231 (1964).
4. W. Byers Brown, J. Chem. Phys., 44, 0000 (1966).
5. J. M. Robinson, Jr., Ph. D. Thesis, University of Texas, Austin (1957).
6. D. P. Chong and Y. Rasiel, J. Chem. Phys., 44, 0000 (1966).
7. J. C. Browne and F. A. Matsen, Phys. Rev., 135A, 1227 (1964).
8. J. O. Hirschfelder, W. Byers Brown and S. T. Epstein, Advances in Quantum Chemistry 1, 255 (ed. Lowdin, Academic Press, New York, 1965)
9. Some of the 28 terms are required by symmetry to have the same coefficients, so that the number of degrees of freedom is actually less than 27.
10. See Eq. (23) of paper I, reference 4.
11. See Eq. (104) of paper I, reference 4.
12. Note, however, that the calculated values are for the calculated equilibrium distance, and have not been averaged over the vibrational motion.
13. The expectation values of $r\cos\theta$ and $r^{-2}\cos\theta$ are essentially the dipole moment and forces, and are given in Tables I and II.

a. L. Wharton, L. P. Gold and W. Klemperer, J. Chem. Phys., 37, 2149 (1962).

14. Physical constants have been taken from Physics Today, 17, 48 (1964).

TABLE I Results for Single Constraints (atomic units)

	Free variation	$\mathcal{H} = \mathcal{T}_L$	$\mathcal{H} = \mathcal{T}_H$	$\mathcal{H} = \mathcal{T}$	$\mathcal{H} = \mathcal{V}$	Exact
λ	—	4.106×10^{-4}	1.209×10^{-4}	4.117×10^{-4}	-1.765×10^{-4}	-
ΔE	—	2.93×10^{-6}	4.51×10^{-9}	2.95×10^{-6}	2.22×10^{-7}	-
$\langle \mathcal{T}_L \rangle$	0.014251	(-3×10^{-12})	0.014283	7.005×10^{-7}	0.014280	0
$\langle \mathcal{T}_H \rangle$	7.461×10^{-5}	1.836×10^{-4}	(2×10^{-15})	-7.005×10^{-7}	3.521×10^{-5}	0
$\langle \mathcal{T} \rangle$	0.014326	1.836×10^{-4}	0.014283	(8×10^{-13})	0.014315	0
$\langle \mathcal{V} \rangle / E$	3.12×10^{-4}	3.19×10^{-4}	3.09×10^{-4}	3.08×10^{-4}	(0)	0
Dipole moment (Debyes)	5.8887	5.8866	5.8885	5.8857	5.8882	5.882 ± 0.003 [a]

TABLE II

Results for double constraints (atomic units)

	$\mathcal{F}_H$ and $\mathcal{F}_L$	$\mathcal{F}$ and $\mathcal{V}$	$\mathcal{F}_L$ and $\mathcal{V}$	$\mathcal{F}_H$ and $\mathcal{V}$
λ_1	2.987×10^{-4}	4.111×10^{-4}	4.111×10^{-4}	5.737×10^{-5}
λ_2	4.129×10^{-4}	1.740×10^{-4}	-1.804×10^{-4}	-1.756×10^{-4}
ΔE	2.95×10^{-6}	3.16×10^{-6}	3.16×10^{-6}	2.23×10^{-7}
$\langle \mathcal{F}_L \rangle$	—	1.087×10^{-4}	(2.2×10^{-13})	0.014295
$\langle \mathcal{F}_H \rangle$	—	-1.087×10^{-4}	1.436×10^{-4}	$(< 10^{-14})$
$\langle \mathcal{F} \rangle$	-4.5×10^{-13}	(7.1×10^{-13})	1.436×10^{-4}	0.014295
$\langle \mathcal{V} \rangle / E$	3.11×10^{-4}	—	—	—
Dipole moment (Debyes)	5.8859	5.8851	5.8860	5.8880

TABLE III

OTHER PROPERTIES[14]

	Free Variation	$\mathcal{H} = \mathcal{V}$	$\mathcal{J}$ and $\mathcal{V}$
$10^6 \chi(\mathrm{Li})^d$, $\mathrm{cm}^3\ \mathrm{mole}^{-1}$	-21.1731	-21.1719	-21.1699
$10^6 \chi(\mathrm{H})^d$, $\mathrm{cm}^3\ \mathrm{mole}^{-1}$	-24.6905	-24.6953	-24.6943
$\sigma(\mathrm{Li})^d$, ppm	107.751	107.752	107.768
$\sigma(\mathrm{H})^d$, ppm	39.220	39.218	39.220
Molecular quadrupole moment (Buckinghams)	-4.1488	-4.1468	-4.1458
Electric field gradient q(Li) (a.u.)	-0.038765	-0.038914	-0.038923

TABLE A

Wave function coefficients, $R = R_e(calc) = 3.046$ Bohr

j	c_j	j	c_j
1	+0.12748	15	-0.00039
2	-0.11210	16	-0.00023
3	+0.15574	17	-0.07270
4	-0.01442	18	-0.02977
5	+0.01379	19	+0.10016
6	+0.02287	20	-0.25955
7	+0.00530	21	-0.00217
8	+0.00331	22	+0.00216
9	-0.00331	23	-0.01501
10	+0.00466	24	+0.15098
11	-0.00462	25	-0.04601
12	-0.00057	26	+0.13318
13	0.00095	27	-0.03624
14	-0.00327	28	-0.00101