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On the use of dipole moment as a collective coordinate in constrained variational calculations

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Abstract. The dipole moment function of a diatomic molecule may be viewed as a continuous collective coordinate which encodes a lot of information about sharing of electrons between the atoms concerned. By its very nature it takes cognizance of certain many-body effects and should shape the constrained wavefunction or the one electron density in much the same way as would explicit inclusion of the same many-body effects. A case study of the problem with lithium hydride as the model system has been presented and the long range behaviour of the constrained density analysed. The spectrum of the constrained Fock operator is compared with that of the unconstrained one.

Keywords. Constrained variation; direct determination of density; penalty function method; dipole moment as a collective coordinate.

1. Introduction

The variational method is a very useful technique in atomic and molecular calculations of electronic structure and properties. Among the properties of a system, energy has a special status in that it is always estimated one order of magnitude better than the other non-commuting observables. Energy, therefore can *not* reflect the *error* in an approximate variational wavefunction as much as the other properties (observables $\{\hat{A}_k\}$ not commuting with $\hat{H}$). The constrained variational method (CVM) was developed in this context. Essentially what one does in CVM is try to minimize energy subject to the minimization of errors in the expectation values of number of chosen observables (Mukherjee and Karplus 1963; Rasiel and Whitman 1965; Chong and Rasiel 1966) without increasing the variational flexibility of the trial wavefunction any further from that already present in the unconstrained trial function. This, however, entails some sacrifice in energy (Byers Brown 1966). The particular choice of constraining observables is conditioned by the purpose at hand. Thus, if one wishes to use the constrained wavefunction as an alternative starting point in a configuration interaction or perturbative calculation with a view to accelerating the convergence, a property which delicately depends on the behaviour of the wavefunction close to the nucleus is the obvious choice. Alternatively one may use the nuclear cusp condition as a suitable theoretical constraint on the wavefunction. For some other purposes, experimental values of electric dipole moment, quadrupole moment etc could be useful. Of the different observables the dipole moment (μ_{AB}) of a diatomic species AB offers some interesting possibilities as a constraining parameter. These possibilities hinge on the fact that μ_{AB} can be treated as a continuous collective coordinate (right from the united atom to the separated atom limit) which has encoded in it very significant information concerning the sharing of electron density between the atom-pair (A, B) and deformation of the atomic density on molecule formation. By its very nature $\mu_{AB}(R)$ takes into account certain many-body effects and when used as a constraint would possibly shape the constrained wavefunction or the one-electron density in much the same way as explicit inclusion of these effects would have done. Hence, if the dipole moment function $\mu_{AB}(R)$ of AB in a particular electronic state (say, the ground state) be known, it can be used as a constraint to obtain what may be called a dipole constrained potential energy curve. A question of immediate interest concerns the type and the extent of reorganization of electron density induced by the constraint over the whole range of R and particularly in the large R regions. More interestingly, one may think of treating the internuclear separation R_{AB} and $\theta_{AB}(\theta_{AB} = \mu_{AB}/R_{AB})$ as two independent collective coordinates and try to obtain an energy map in the (R, θ) plane. Among other things, these maps can throw light on the existence of metastable states, nature of bonding or existence of alternative channels of dissociation, if any (viz $A+B$, $A^{+}+B^{-}$, $A^{+2}+B^{-2}$ etc). The basic purpose of the present work is to investigate some of the aforementioned possibilities.

2. The problem

The system of our choice is the lithium hydride molecule. The ground state dipole moment curve of lithium hydride is known quite accurately (Patridge and Langhoff 1981). The special feature of the μ-R profile of lithium hydride lies in an inversion displayed by it. The absolute value of μ_{LiH} first increases, attains a maximum and decays to zero as $R \rightarrow \infty$. This inversion followed by a decay to zero value cannot be recovered in a single configuration SCF calculation, *ab initio* or semiempirical. Obviously, this is related to the basic inadequacy of the single configuration description of the wavefunction. Could a μ-constrained calculation at the Hartree-Fock level generate the correct μ-R profile and simultaneously improve the quality of the wavefunction or the one-electron density in the large-R regions? We investigate these questions in what follows. The calculations are made at an all valence semiempirical (CNDO/2) level of approximation and the constrained variational calculations are carried out by using a method for the direct determination of constrained pure state electron density in a discrete orthonormal basis developed by us (Das and Bhattacharyya 1986; Das *et al* 1985).

3. The method

Let us consider a $2m$-electron closed-shell molecule described in terms of a one-electron density matrix P in an n-dimensional discrete orthonormal basis $\{\chi_i\}_{i=1,n}$. We demand that in addition to the N-representability constraints on P ($P^2 = P$, $P^+ = P$ and $Trp = m$) there is an additional constraint that P must minimize energy subject to the condition that

$$2\,\mathrm{Tr}\{PD\} = d_0, \tag{1}$$

where D represents the electric dipole matrix in the χ-basis and d_0 is the actual (known) dipole moment of the system. The variational determination of P subject to the constraint in (1) can be done in a number of ways. The general strategy for handling a problem of this kind, recently developed by us (Das and Bhattacharyya 1986) requires a start, in the present case, with the functional $\varepsilon(E, E_L, \sigma, \lambda; P)$, where

$$\varepsilon(E, E_L, \sigma, \lambda; P) = (E-E_L)^2 + \sigma \mathrm{Tr}(P^2-P)^2 + \lambda[\mathrm{Tr}\{PD\}-d_0]. \quad (2)$$

In (2), σ is a penalty weight factor of appropriate dimension and magnitude, λ is the Lagrangian multiplier connected with the constraint in (1) and E_L is an estimated lower bound to the constrained energy. Minimization of ε leads to the following iterative scheme for the determination of P:

$$P_{i+1} = 3P_i^2 - 2P_i^3 - \alpha(E_i - E_L^i)F_i - \gamma_i D, \quad (3)$$

where $\alpha = 2/\sigma$ and $\gamma = \lambda/\sigma$ and

$$F_i = h + G(P_i);\ G(P_i) = 2J(P_i) - K(P_i).$$

The Lagrangian parameter γ_{i+1} is determined by the condition

$$2\mathrm{Tr}\{P_{i+1}D\} = d_0, \quad (4)$$

which leads to the result that

$$\gamma_{i+1} = 2[\mathrm{Tr}\{Q_i D\} - d_0]/\mathrm{Tr}\{D^2\}, \quad (5)$$

where,

$$Q_i = 3P_i^2 - 2P_i^3 - \alpha(E_i - E_L^i)F_i.$$

The $(i+1)$th approximation to the lower bound E_L^{i+1} can be obtained by adopting the method of Fiacco and McCormik (1968), which in the present case takes the following form

$$E_L^{i+1} = E_L^i - \beta \mathrm{Tr}\{A_i^\dagger A_i\}^{1/2},\ (0 < \beta \leqslant 1), \quad (6)$$

where,

$$A_i = \alpha(E_i - E_L^i)F_i + (2P_i^3 - 3P_i^2 + P_i) + \gamma D.$$

The iterations represented by (3) were terminated when $\mathrm{Tr}\{A_i^\dagger A_i\} < 10^{-6}$ in each calculation.

4. Results and discussion

4.1 *Large-R behaviour of the constrained density*

The constrained calculations correctly reproduce all the details of the actual μ-R profile (table 1) including the inversion at the correct value of R. We have already reported that the force constant improves remarkably (Das *et al* 1987) due to the constraint. In the present study, our main interest lies in the large-R behaviour of the constrained density. Table 2 summarises variations in the net charge density on lithium and hydrogen atoms over a large range of internuclear separation both in

Table 1. Comparison of the actual ground state dipole moment function of LiH with those predicted by the unconstrained and the μ-constrained Hartree-Fock (semiempirical) methods.

R (a.u.)	μ Hartree-Fock (Debye)	μ Constrained HF (Debye)	μ Actual (Debye)
1·75	6·86	4·837	4·840
2·00	6·85	4·946	4·950
2·25	6·75	5·11	5·11
2·50	6·59	5·31	5·31
2·75	6·39	5·55	5·56
3·00	6·15	5·81	5·81
3·25	5·88	6·08	6·08
3·50	5·60	6·35	6·35
4·00	4·97	6·88	6·88
5·00	3·54	7·56	7·56
5·56	2·77	7·48	7·48
6·00	1·96	6·93	6·93
8·00	1·48	1·97	1·97
10·00	4·97	0·05	0·05

Table 2. Comparison of constrained and unconstrained charge densities on Li and H atoms at various internuclear separations of Li–H.

$R_{\mathrm{Li\ H}}$ (a.u.)	Unconstrained HF results: net charge density on		Constrained Hartree-Fock results: net charge density on	
	Li atom	H atom	Li atom	H atom
2·00	0·2632	− 0·2632	0·3776	− 0·3776
2·75	0·2678	− 0·2678	0·3139	− 0·3139
3·00	0·2715	− 0·2715	0·2896	− 0·2896
3·75	0·2873	− 0·2873	0·2235	− 0·2235
4·50	0·3078	− 0·3078	0·1742	− 0·1742
5·00	0·3226	− 0·3226	0·1552	− 0·1552
5·50	0·3370	− 0·3370	0·1506	− 0·1506
7·00	0·3694	− 0·3694	0·2240	− 0·2240
8·00	0·3844	− 0·3344	0·2750	− 0·2750
10·00	0·3858	− 0·3858	0·2530	− 0·2530

the unconstrained and the μ-constrained descriptions of the molecule. The constrained calculations are seen to predict a higher degree of polarity of the Li–H molecule at shorter values of $R (R < R_0)$ compared to the polarity in the unconstrained description. But as R increases, the constraint effectively forces more and more electron density to flow from H → Li (compared to the unconstrained results) signifying that the constrained potential energy curve is a better one and may perhaps lead to the correct dissociation limit. A perusal of table 2 clearly shows that although the polarity of the Li–H molecule is far less in the constrained description at all the larger values of R, the polarity does not decrease monotonically as $R \rightarrow \infty$. It decreases monotonically upto a certain value of $R (= R_c$, say). Beyond $R = R_c$, Li → H transfer of electron density (compared to that observed for $R < R_c$) seems to increase progressively (table 2) even in the constrained calculations, although the degree of Li → H electron transfer remains far less pronounced compared to that found in the unconstrained Hartree-Fock description. The constrained dipole moment, however, vanishes beyond $R > 10{\cdot}0$ a.u. as demanded. This failure of the constrained PE curve to lead to the correct dissociation limit (Li + H) even though the *limiting zero dipole moment value is correctly reached* may appear to be intriguing at first sight. But it arises quite naturally due to the following reason. Within the framework of our basic approximations (CNDO/2), the ground state dipole moment of LiH can be resolved into two separate contributions: (a) that due to charge separation in the molecule (μ_{charge}); (b) that due to the mixing or hybridization of $2s$ and $2p_z$ basis function on the Li atom (this destroys the spherical symmetry of the Li-electron density) (μ_{hyb}). The zero dipole moment in the large R-limit ($R > 10$ a.u.) is reached in the constrained calculation not by forcing μ_{charge} and μ_{hyb} to vanish separately, but by forcing them to cancel each other as the internuclear separation increases beyond a particular value ($R = 10$ a.u.). The μ-constrained dissociation limit of Li–H is thus different from both the unconstrained Hartree–Fock and the actual dissociation limits. In table 3 we have compared the constrained and unconstrained densities at $R = 10.0$ a.u. It is clear that the (i) net charge separation in the constrained case is less than that in the constrained one, (ii) $2s - 2p$ mixing of Li orbitals in the constrained case is larger than its unconstrained counterpart; (iii) an enhanced electron population in the lithium $2p_\sigma$ orbital is found in the constrained calculation compared to the unconstrained one. Apparently therefore, the dissociation limit in the constrained one-configuration calculation has higher weightage of products like Li ($2p$) compared to what one finds in the HF dissociation limit and of course, a lesser degree of weightage of the ionic products like Li^+ and H^-. The use of the additional constraint, $\mu_{\text{hyb}} = 0$, for all values of R may possibly bring about the correct homopolar dissociation. This is being explored at present. Thus although the collective coordinate for a diatomic molecule does possess very significant information about electron sharing between the atoms A and B at various internuclear separations, it can *not* as such recover the correct dissociation limit when used as the *only* constraining observable if one works in the framework of single determinant representable densities. However, it does modify the dissociation limit. It may be possible therefore to use θ as a collective coordinate in the construction of an energy map in the (R, θ) plane and it

Table 3. Comparison of the unconstrained (i.e. Hartree-Fock) and the μ-constrained electron densities for Li–H in the ground state at a large internuclear separation ($R = 10{\cdot}0$ a.u.).

Atom/basis function		Electron density (χ_i)		Degree of $2s - 2p_z$ mixing on Li-atom	
(A)	(χ_i)	HF results	CHF results	HF results	CHF results
Li/	$2s$	0·5194	0·6126	0·2220	0·2870
	$2p_x, 2p_y(\pi)$	0·0	0·0		
	$2p_z(\sigma)$	0·0956	0·1344		
H/	$1s$	1·3850	1·2530		

may reveal new information on the existence of metastable states of the diatomic system used.

4.2 *Constrained versus unconstrained orbitals*

The set of orbitals $\{\phi_i^0\}$ that diagonalise the unconstrained minimum energy idempotent one-electron density matrix (P_0) are the Hartree-Fock orbitals (HFO). The orbital set that diagonalises the constrained idempotent one-electron density matrix (P_c) represent a set of natural orbitals $\{\phi_i^c\}$ which may be called the constrained Hartree-Fock orbitals (CHFO). $\{\phi_i^0\}$ diagonalises the unconstrained Fock operator $F^0 (F^0 \phi_i^0 = \phi_i^0 \varepsilon_i^0;\ F^0 = h + \nu_{\mathrm{HF}}(\phi_i^0)$. Similarly, $\{\phi_i^c\}$ satisfy the following eigenvalue equation

$$F^c \phi_i^c = \phi_i^c \varepsilon_i^c,$$

where

$$F^c = h + \nu_{\mathrm{HF}} \{\phi_i^c\}.$$

One may use the set $\{\phi_i^c,\ \varepsilon_i^c\}$ as an alternative starting point in perturbative or *CI* calculations of energy or other properties, may be, with better convergence properties. To have some idea about the disposition of the spectrum of the constrained and the unconstrained Fock operators we have compared in table 4 the HFO and CHFO for lithium hydride at $R = 7.0$ a.u. A perusal of table 4 clearly reveals that the 3σ MO is more localised on the hydrogen atom in the unconstrained calculation than predicted by the dipole constrained approximation. The two unoccupied σ orbitals (4σ, 5σ) are also affected by the constraint, albeit indirectly. The corresponding orbital energies indicate that the constraint stabilises 3σ and 4σ orbitals (relative to the unconstrained ones) but destabilises all other

Table 4. A comparison of the eigenspectrum of the unconstrained and the constrained Fock operator for lithium hydride molecule at $R = 7{\cdot}00$ a.u. The calculations were done at a semiempirical level (CNDO/2) using dipole moment as the constraint.

MO/AO basis		Unconstrained AO amplitudes	Unconstrained orbital energy	Constrained AO amplitudes	Constrained orbital energy
(ϕ_i)	(χ_p)	(C_{pi}) in ϕ_i^0	ϵ_i^0	(C_{pi}) in ϕ_i^c	ϵ_i^c
3σ Li	$2s$	0·4522		0·4949	−0·2878
	$2p_z$	0·3320	−0·2603	0·3783	
	$2p_x$, $2p_y$	0·0,0·0		0·0, 0·0	
H	$1s$	0·8275		0·7823	
4σ Li	$2s$	0·8917			
	$2p_z$	−0·1488	−0·0328	0·8101	−0·0332
π	$2p_x$, $2p_y$	0·0,0·0		0·1248	
			0·0371,0·0371	0·0,0·0	
H	$1s$	−0·4275		-0·5728	
Li	$2p_x$, $2p_y$	1·0,1·0	0·0371, 0·0371	1·0,1·0	0·0506, 0·0506
5σ Li	$2s$	−0·1920		−0·3143	
	$2p_z$	0·9312		0·9172	
	$2p_x$, $2p_y$	0·0,0·6		0·0, 0·0	
H	$1s$	−0·3641	0·0466	−0·2447	0·0513

unoccupied orbitals. The constraint therefore shifts the entire spectrum of F^c relative to F^0. Clearly, the rate of convergence of a perturbative series or *CI* expansion will be different when $\{\phi_i^c, \varepsilon_i^c\}$ are used as basis functions. However, a priori theoretical analysis of the effects of a particular constraint on the rate of convergence of the corresponding perturbative or *CI* series is a formidable task and is being studied at present. We hope to return to this aspect in the near future.

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