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Constrained Variations for Diatomic Forces and Force Constants

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The results of earlier studies of diatomic forces and force constants are used to formulate force constraints. It is proposed that such constrained variations should improve force constant calculations.

Mittels früherer Ergebnisse für Bindungskräfte bei zweiatomigen Molekülen werden Nebenbedingungen für die Wellenfunktion formuliert. Es ist anzunehmen, daß dies zu einer Verbesserung der Berechnung für die entsprechenden Kraftkonstanten führt.

Les résultats d'études antérieures des forces et des constantes de force diatomiques sont utilisés pour formuler des contraintes de force. De telles variations contraintes devraient améliorer les calculs de constante de force.

1. Introduction

On one hand, the subject of diatomic forces and force constants has been extensively studied by various workers [1–3]. On the other hand, the method of constrained variations has been well developed [4–11]. The object of this paper is to formulate a variety of constraints which can be imposed on electronic wavefunctions in order to improve force constant calculations.

No attempt is made in this paper to review the literature on diatomic forces and force constants or on the closely related virial and electrostatic theorems. Instead, we make use of the results of Salem [1], Benston and Kirtman [2], and Benston [3], and recast them in operator form suitable for use in constrained variations.

Let $U(R)$ represent the potential energy for the motion of the nuclei as a function of the internuclear distance R. *A priori* determination of force constants[1] involves calculation of (a) three points on the U curve, (b) two points on the dU/dR curve, or (c) one point on the d^2U/dR^2 curve, namely at the equilibrium separation R_e.

2. Energy

The most common practice by far is to use method (a), although method (c) has sometimes been chosen [1, 2].

Following previous workers, we use the (adiabatic) Born-Oppenheimer approximation and consider a spinless Hamiltonian

$$H = T + V, \tag{2.1}$$

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[1] The term "force constant" in this paper implies the quadratic force constant. Computation of cubic force constants would require an additional point in each case.

where
$$T = -1/2 \sum_i \nabla_i^2 , \tag{2.2}$$

$$V = Z_A Z_B / R - \sum_i [(Z_A / r_{iA}) + (Z_B / r_{iB})] + \sum_{i<j} r_{ij}^{-1} , \tag{2.3}$$

and the symbols have the usual meanings. Atomic units are used throughout: a_0 for lengths, e^2/a_0 for energies, e^2/a_0^2 for forces, and e^2/a_0^3 for force constants. In the coordinate system adopted in this paper, the diatomic molecule AB lies on the z-axis with $z(\mathrm{B}) - z(\mathrm{A}) = R$. The angle θ_{iA} is $\sphericalangle i\mathrm{AB}$ and θ_{iB} is the supplement of $\sphericalangle i\mathrm{BA}$.

In the Born-Oppenheimer approximation, the energy E of the electronic wavefunction is determined from the Hamiltonian of Eq. (2.1) as a function of R; $E(R)$ is then considered as $U(R)$. Method (a), therefore, involves fitting the calculated $E(R)$ to a polynomial in R. The worker optimistically assumes that the fitted curve is parallel to the exact potential. This basic assumption has little theoretical basis and is, in fact, invalid when the dissociation limit is not proper, as in the case of many self-consistent field wavefunctions. We feel that method (a) is, therefore, poor, except perhaps with very accurate wavefunctions.

Since we cannot find explicit theoretical constraints to force the calculated energy curve to be parallel to the exact potential, this approach will not be considered further in this paper.

3. Diatomic Forces

Following Benston and Kirtman [2], we write the energy of the electronic wavefunction as
$$E = \langle \psi | H | \psi \rangle , \tag{3.1}$$
where ψ is assumed to be normalized. Then,
$$dE/dR = \langle \psi | (\partial H / \partial R)_q | \psi \rangle + 2 \langle (\partial \psi / \partial R)_q | (H - E) | \psi \rangle , \tag{3.2}$$
where q represents an arbitrary set of electronic coordinates. If
$$\langle (\partial \psi / \partial R)_q | (H - E) | \psi \rangle = 0 , \tag{3.3}$$
then
$$dE/dR = \langle \psi | F_q | \psi \rangle , \tag{3.4}$$
where F_q has been used to replace $(\partial H / \partial R)_q$ and represents the attractive force operator. Eq. (3.4) is the well-known generalized Hellmann-Feynman theorem, and is obviously satisfied by exact wavefunctions. For approximate wavefunctions, the condition expressed in Eq. (3.3) poses no difficulties in principle, since an approximate wavefunction can be made to satisfy the condition by phase variations [12, 13] or by constrained variations [4–7].

Benston and Kirtman [2] studied two sets of q. One set of electronic coordinates, which preserves the angles θ_{iA} and θ_{iB}, is called scaled electron coordinates and denoted by a subscript s. Their result can be written as
$$F_s = -(2T + V)/R , \tag{3.5}$$
which is just the operator appearing in the familiar virial theorem for diatomic molecules.

Another set, which they called fixed electron coordinates and denoted by a subscript f, preserves the electronic coordinates measured along space-fixed axes.

However, since the origin of the space-fixed axes is arbitrary, the operator F_f can take on several forms. From the results of Salem [1], one can readily get

$$F_{\mathrm{A}} = -Z_{\mathrm{A}}Z_{\mathrm{B}}/R^2 - Z_{\mathrm{B}} \sum_i \cos\theta_{i\mathrm{B}}/r_{i\mathrm{B}}^2\,, \tag{3.6}$$

$$F_{\mathrm{B}} = -Z_{\mathrm{A}}Z_{\mathrm{B}}/R^2 + Z_{\mathrm{A}} \sum_i \cos\theta_{i\mathrm{A}}/r_{i\mathrm{A}}^2\,, \tag{3.7}$$

$$F_M = \frac{1}{2}(F_{\mathrm{A}} + F_{\mathrm{B}})\,, \tag{3.8}$$

where F_{A}, F_{B} and F_M are the various forms of F_f when nucleus A, B, and the midpoint of AB are held fixed respectively. The operator F_{A} is the operator for the attractive force on nucleus B; and F_{B}, that on A. Benston and Kirtman [2] placed the origin at the center of mass and their result can be rewritten as

$$F_c = \mu F_{\mathrm{A}} + (1-\mu)F_{\mathrm{B}}\,, \tag{3.9}$$

where

$$\mu = M_{\mathrm{B}}/(M_{\mathrm{A}} + M_{\mathrm{B}})\,, \tag{3.10}$$

and M_{A} and M_{B} are the atomic masses.

In a later paper, Benston [3] considered still another set of electronic coordinates, denoted by a subscript z. It represents the space-fixed x, y, and $z' = z/R$ coordinates of the electron. She obtained

$$\begin{aligned} F_z = -Z_{\mathrm{A}}Z_{\mathrm{B}}/R^2 + R^{-1}\Big[&\sum_i \partial^2/\partial z_i^2 \\ &+ \sum_i (Z_{\mathrm{A}}\cos^2\theta_{i\mathrm{A}}/r_{i\mathrm{A}} + Z_{\mathrm{B}}\cos^2\theta_{i\mathrm{B}}/r_{i\mathrm{B}}) - \sum_{i<j}(z_i - z_j)^2/r_{ij}^3\Big]\,. \end{aligned} \tag{3.11}$$

Thus, we see that there are at least six ways of calculating diatomic forces. With approximate wavefunctions, different forms of the force operator generally lead to different numerical results[2]. This undesirable ambiguity is reminiscent of the analogous situation in the case of oscillator strengths, where the ambiguity can be removed by constrained variations [8, 9]. When we use method (b) to calculate force constants, we hope to get good values for the forces. Hence, we propose the use of constrained variations [4–7] in order to eliminate the ambiguity mentioned above and to obtain hopefully better values for diatomic forces. The constraint operators are simply

$$F_{pq} = F_p - F_q\,, \tag{3.12}$$

where p and q can be any pair among s, A, B, M, C, and z. It should be noted that the constraint $\langle F_{\mathrm{AB}}\rangle = 0$ would make

$$\langle F_{\mathrm{A}}\rangle = \langle F_{\mathrm{B}}\rangle = \langle F_M\rangle = \langle F_C\rangle \tag{3.13}$$

and is a natural one to use for heteronuclear diatomic molecules. Another constraint one can easily impose is $\langle F_{s\mathrm{A}}\rangle = 0$. The solution of the resulting constrained secular equation by perturbation [4–6] or by parametrization [5] has been shown to be straightforward.

4. Diatomic Force Constants

The diatomic force constant can be expressed in terms of an operator

$$k = (d^2E/dR^2)_{R_e} = \langle\psi|K|\psi\rangle_{R_e}\,. \tag{4.1}$$

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[2] For homonuclear diatomic molecules, $\langle F_{\mathrm{A}}\rangle = \langle F_{\mathrm{B}}\rangle = \langle F_M\rangle = \langle F_C\rangle$ automatically.

Differentiating Eq. (3.2), one gets[3]

$$K_{qq'} = (\partial^2 H/\partial R^2)_{qq'} + 2(F_q - \langle F_q \rangle)(\partial/\partial R)_{q'}, \tag{4.2}$$

if Eq. (3.3) holds or if the weaker condition:

$$(d/dR)\,\langle(\partial\psi/\partial R)_q|(H-E)|\psi\rangle = 0 \tag{4.3}$$

is satisfied. It should be noted that, if R_e is determined by the energy curve, $\langle F_q \rangle$ may not be zero even at R_e but can be made to vanish by constrained variations [4–7].

Because there are so many sets of q, one has even more different forms of the operator $K_{qq'}$. Some[4] of these can be obtained from the results of Salem [1] and Benston and Kirtman [2]; some are unpublished; and the rest are yet to be derived.

It is obviously undesirable to obtain different values for the same quantity k when different forms of $K_{qq'}$ are used. Again, this ambiguity can be removed by means of constrained variations. The constraint operators, in this case, are

$$K_{pp'qq'} = K_{pp'} - K_{qq'}. \tag{4.4}$$

5. Discussions

The early papers [4–7] on constrained variation were concerned with the method: that is, the formulation of the constrained variation principle and the solution of the constrained secular equation. The purpose of constrained variations has been found in recent studies [8–11]. The present paper adds to the latter. We feel that the method of constrained variations has finally come of age.

Both the force constraints and force constant constraints are expected to improve force constant calculations. In principle, none of the necessary integrals involved should be insurmountably difficult for diatomic molecules. Both the transformation to elliptical coordinates and numerical quadrature, where necessary, have been well worked out. In practice, force constraints, except those involving F_z, are much easier to impose.

The idea of force constraints is not new. We have applied the constraint $\langle F_{AB} \rangle = 0$ to the lithium hydride molecule [6], but only at the theoretical R_e. We plan to apply force constraints to force constant calculations in the near future.

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[3] Compare with Eq. (13) of Ref. [2].

[4] Such as K_{MM}, K_{BB}, K_{AB}, K_{ss}, K_{sf}, and K_{ff}.

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