

Enhanced procedure for the refinement of kinetic and potential functions for large-amplitude vibrations

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An enhanced method for the refinement of kinetic and potential terms for large-amplitude vibrations has been shown. To ensure the search for a minimum, the quadratic error between the observed and calculated energy levels is minimized with a quasi-Newton algorithm using a positive-definite Hessian matrix. In addition, analytical derivatives are obtained for computation of the gradient vector.

Recently, a method for the refinement of kinetic and potential terms for large-amplitude vibrations has been proposed.¹ This method minimizes the square difference, *i.e.* the error, between the observed and calculated energy levels using a quasi-Newton approach. The method is second order with respect to the Taylor expansion of the error. This represents an advantage over a classical least-squares refinement as the convergence is faster. In the original implementation² the minimization procedure did not impose a positive definiteness to the Hessian. Thus, we cannot be sure of searching for a minimum. In addition, the gradients were calculated numerically. These facts translate to large amounts of computation time when several large-amplitude vibrations are considered. In this work we present a way of overcoming these limitations.

The first step is to obtain analytical expressions for the derivatives of the error. The calculated energy levels are obtained from the following pure vibrational hamiltonian for n large-amplitude vibrations³

$$\hat{H} = \sum_i^n \sum_j^n \left[B_{ij} \frac{\partial^2}{\partial q_i \partial q_j} + \left(\frac{\partial}{\partial q_i} B_{ij} \frac{\partial}{\partial q_j} \right) \right] + V(q_1, \dots, q_n) \quad (1)$$

where B_{ij} are the kinetic terms, V is the potential and q_i and q_j represent vibrational coordinates. The previous expression accounts for the non-commutability of the B_{ij} elements and the momentum, $\partial/\partial q_i$, operator. The kinetic B_{ij} terms and the potential, V , are obtained by expanding them in a Fourier or Taylor series on the vibrational coordinates. This hamiltonian is variationally solved using free rotor and/or harmonic oscillator basis functions for each vibration, depending on the boundary conditions.⁴ The matrix elements for the hamiltonian are

$$h_{ij} = \langle \phi_i | \hat{T} + \hat{V} | \phi_j \rangle \quad (2)$$

where ϕ represents the basis functions expressed as

$$\phi_i = \prod_j^n g_{ij} \quad (3)$$

In eqn. (3), g represents free rotor or harmonic oscillator eigenfunctions.

The kinetic and potential contributions are obtained by substitution of eqn. (1) and (3) into eqn. (2).^{4(a)} The kinetic elements are, for $i \neq j$

$$\langle \phi_m | \hat{T} | \phi_n \rangle = \sum_i^n \sum_j^n \sum_k^{N_B} B_{ijk}^0 [\langle g_{mi} | f_{ijki} | g'_{ni} \rangle \langle g_{mj} | f_{ijkj} | g'_{nj} \rangle + \langle g_{mi} | f'_{ijki} | g_{ni} \rangle \langle g_{mj} | f_{ijkj} | g'_{nj} \rangle] \prod_{p \neq i, j}^n \langle g_{mp} | f_{ijkp} | g_{np} \rangle \quad (4)$$

Whereas for $i = j$ we have

$$\langle \phi_m | \hat{T} | \phi_n \rangle = \sum_i^n \sum_k^{N_B} \left(B_{iik}^0 \langle g_{mi} | f_{iiki} | g''_{ni} \rangle + \langle g_{mi} | f'_{iiki} | g'_{ni} \rangle \right) \prod_{p \neq i}^n \langle g_{mp} | f_{iikp} | g_{np} \rangle \quad (5)$$

The potential contribution is obtained as

$$\langle \phi_m | \hat{V} | \phi_n \rangle = \sum_i^{N_v} V_i^0 \prod_p^n \langle g_{mp} | f_{ip} | g_{np} \rangle \quad (6)$$

In the previous equations f represents the polynomic or trigonometric terms in the Fourier or Taylor expansions of B_{ij} and V .

After calculation of the energy levels, the refinement is applied by computing a quadratic error function, S .

$$S(\mathbf{C}) = \sum_i^{n_e} (\varepsilon_i^c - \varepsilon_i^o)^2 \quad (7)$$

In eqn. (7), the index runs on the considered energy levels, ε^c represents the calculated energy levels and ε^o the observed values. In addition, \mathbf{C} is a vector formed by the kinetic, B_{ij} , and the potential, V_i , terms. Expanding the error in a second-order Taylor series on the \mathbf{C} parameters, we obtain

$$\nabla S(\mathbf{C}_{n+1}) = \nabla S(\mathbf{C}_n) + H(\mathbf{C}_n) \cdot \mathbf{q}(\mathbf{C}_n) \quad (8)$$

where $\nabla S(\mathbf{C})$ is the gradient of $S(\mathbf{C})$ with respect to \mathbf{C} , $H(\mathbf{C}_n)$ is the Hessian of $S(\mathbf{C})$, and \mathbf{q} is $\mathbf{C}_{n+1} - \mathbf{C}_n$. Considering \mathbf{C}_{n+1} to be a minimum we get

$$\mathbf{C}_{n+1} = \mathbf{C}_n - H(\mathbf{C}_n)^{-1} \cdot \nabla S(\mathbf{C}_n) \quad (9)$$

Eqn. (9) represents an iterative technique for the location of the minimum.

The gradient components of the error are defined as

$$\nabla S_j = [\partial S(\mathbf{C}) / \partial C_j] \quad (10)$$

and the gradient with respect to some kinetic or potential term, C_j , is obtained as

$$(\partial S/\partial C_j) = 2 \sum_i^{n_e} (\epsilon_i^c - \epsilon_i^o) \cdot (\partial \epsilon_i^c/\partial C_j) \quad (11)$$

In eqn. (11) the derivatives of the calculated energy levels define the Jacobian matrix, J , whose elements are

$$J_{ij} = (\partial \epsilon_i^c/\partial C_j) \quad (12)$$

Thus, from eqn. (12) and using energies relative to the first, ϵ_0 , energy level, we obtain

$$J_{ij} = \langle \Psi_i | \partial \hat{H}/\partial C_j | \Psi_i \rangle - \langle \Psi_0 | \partial \hat{H}/\partial C_j | \Psi_0 \rangle \quad (13)$$

with Ψ_i being the eigenfunctions corresponding to the different energy levels obtained in the variational procedure

$$\Psi_i = \sum_m C_m^i \phi_m^i \quad (14)$$

where C_m are the variational coefficients. The analytical J matrix is obtained considering that the derivatives of variational parameters do not appear in the gradient formula.⁵ Therefore, by substitution of eqn. (14) into eqn. (13) we get

$$J_{ij} = \sum_{m \leq n} (2 - \delta_{mn}) C_m^i C_n^i \langle \phi_m^i | \partial \hat{H}/\partial C_j | \phi_n^i \rangle - \sum_{m \leq n} (2 - \delta_{mn}) C_m^0 C_n^0 \langle \phi_m^0 | \partial \hat{H}/\partial C_j | \phi_n^0 \rangle \quad (15)$$

with δ being the Kronecker delta. When Ψ_i and Ψ_0 are expanded on the same basis functions eqn. (15) reduces to

$$J_{ij} = \sum_{m \leq n} (2 - \delta_{mn}) (C_m^i C_n^i - C_m^0 C_n^0) \times \langle \phi_m^i | \partial \hat{H}/\partial C_j | \phi_n^i \rangle \quad (16)$$

Since the hamiltonian is linear on the C parameters, $\partial \hat{H}/\partial C_j$ is easily obtained by making $C_j = 1$ and $C_{i \neq j} = 0$ in eqn. (4)–(6). Substitution of eqn. (15) and (16) into eqn. (11) yields the desired analytical derivatives.

To impose the positive definiteness of the Hessian, H , in each step of eqn. (9), we introduce the BFGS, or positive definite secant, updating algorithm.^{6,7} Thus

$$A_{n+1} = A_n + \frac{q_n^T \cdot q_n}{g_n^T \cdot [A_n \cdot g_n]^T} - \frac{A_n \cdot g_n \cdot [A_n \cdot g_n]^T}{g_n \cdot A_n \cdot g_n} + g_n^T \cdot [A_n \cdot g_n]^T \quad (17)$$

where $A_n = H_n^{-1}$, $q_n = C_{n+1} - C_n$ and $g_n = \nabla S(C_{n+1}) - \nabla S(C_n)$. The BFGS algorithm ensures that the Hessian remains positive definite on all updates. Therefore, we generate a series of search directions that always lower the error given by eqn. (7). The initial Hessian is chosen as a diagonal positive-definite matrix where the diagonal elements are 0.01 times the absolute value of the C_i/g_i ratio.

The BFGS is a locally convergent method, *i.e.*, it will converge to the solution providing it starts close enough to the answer. In the present case, we enhance the minimization including a global convergence strategy. Thus, we introduce a

Table 1 Comparison of the original, case a, and the new, case b, procedures for the refinement of kinetic and potential terms for large-amplitude vibrations

	S_0	T_1
N	5	35
case a	58	31196
case b	52	1322

The table shows the results, in seconds of real time, for the S_0 and T_1 states of acetaldehyde obtained in a DEC Alpha Station 166/200. N represents the number of terms (kinetic + potential) to refine.

parameter, λ , giving the minimum of the function along the search direction.

$$C_{n+1} = C_n - \lambda \cdot H(C_n)^{-1} \cdot \nabla S(C_n) \quad (18)$$

The value of λ is obtained by performing a one-dimensional minimization in the search direction until the new quadratic error is significantly smaller than the previous.⁷

The performance in computation time of the new formulation is compared to the initial one in Table 1. Table 1 shows the results for the two cases used to test the initial formulation,¹ namely, the methyl torsion in the S_0 state of acetaldehyde and the methyl torsion plus carbonyl hydrogen wagging in the T_1 state of acetaldehyde. The results show that for one-dimensional problems the new formulation slightly improves the previous results. However, a dramatic improvement is achieved when the number of vibrations increases and, in consequence, the number of kinetic and potential parameters and the size of the Hamiltonian increase as well. Thus, the new formulation is well suited to the study of several large-amplitude vibrations.

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