A SIMPLE METHOD TO REFINE AB INITIO FORCE FIELDS WITH APPLICATIONS TO CO_2 AND H_2CO

KRISTY L. MARDIS and EDWIN L. SIBERT, *Department of Chemistry and Theoretical Chemistry Institute, University of Wisconsin - Madison, Madison, WI 53706*.

Ab initio methods are now capable of calculating quartic force fields which accurately reproduce experimental observables such as band heads, ν_o and inertial constants, B. We present a method of refining these ab initio force field constants, $\mathbf{f}^{\mathrm{ab}}$. The accuracy of the $\mathbf{f}^{\mathrm{ab}}$ permits the approximation of a figure of merit function,

$$\chi_y^2 = \sum_i \left(y_i^{\mathrm{expt}} - y_i\right)^2 / w_i^2, \quad \text{where } y = \nu_o \text{ or } B, \tag{1}$$

as a Taylor Series truncated at second order,

$$\chi_y^2 \approx A_y^{\mathrm{ab}} + \mathbf{\Upsilon}_y^T(\mathbf{f} - \mathbf{f}^{\mathrm{ab}}) + \frac{1}{2}(\mathbf{f} - \mathbf{f}^{\mathrm{ab}})^T \mathbf{F}_y(\mathbf{f} - \mathbf{f}^{\mathrm{ab}}). \tag{2}$$

Often, the computational effort of minimization is dominated by the derivative calculation. However, calculating ν_o's and B's by Van Vleck perturbation theory facilitates the fast calculation of the Hessian. The merit function is then minimized analytically by diagonalization of this Hessian. This method of improving the force constants has several advantages. First, there is great latitude in choosing a merit function. We choose

$$\chi^2 = (1+\alpha)\chi_{\nu_{\mathrm{O}}}^2 + \alpha\chi_B^2. \tag{3}$$

However, additional terms, such as different isotopic species, can be easily added to the merit function. Second, the calculation of the Hessian provides insight into the contours of the potential energy surface (PES). Third, small eigenvalues, which correspond to long, flat valleys in the PES, can be neglected. Finally, the near quadratic nature of χ^2 permits the minimization to occur in a single step. Specific applications of this method to CO_2 and H_2CO are presented.