

CONVERSION OF *AB-INITIO* FORCE FIELDS AND STRUCTURES TO MOLECULAR MECHANICS ENERGY FUNCTIONS

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Abstract—The rapid development of computers in recent years has brought increasingly complex compounds into the range of high level *ab-initio* calculations. Such calculations produce valuable results which in many cases would be difficult or even impossible to obtain, with comparable accuracy, in any other way (Fogarasi & Pulay, *Annu. Rev. Phys. Chem.* **35**, 191, 1984). Thus, it is highly desirable to be able to utilize these results in the construction of potential energy functions used in molecular mechanics (MM), molecular dynamics and Monte-Carlo calculations. For instance, the significance of quadratic cross terms in MM energy functions is still insufficiently explored (Lii & Allinger, *J. Am. Chem. Soc.* **111**, 8566, 1989). In order to make possible the complete utilization of *ab-initio* results in MM calculations, we have developed a method by which scaled *ab-initio* (or empirical) force fields and structures can be directly converted to MM potential energy parameters, without sacrificing any of the original accuracy with regard to vibrational frequencies or structure. Here we briefly outline the conversion procedure, a more complete analysis being published separately.

INTRODUCTION

In the molecular mechanics method (Pietilä, 1989) the potential energy function may be considered to consist of a quadratic part V_q and a nonquadratic part V_{nq} :

$$V = V_q + V_{nq}, \quad (1)$$

V_{nq} accounts for van der Waals interactions, Coulombic interactions, periodic torsions etc while V_q is the potential energy arising from deformation of valence bonds and angles. Explicitly, V_q can be written:

$$V_q = \frac{1}{2} \sum_{ij} F_{ij}^{MM} (R_i - R_{i0}) (R_j - R_{j0}), \quad (2)$$

where the F_{ij}^{MM} s are called MM force constants, the R_i s are valence coordinates and the parameters R_{i0} define the so-called reference (or intrinsic equilibrium) geometry. In the conversion from *ab-initio* we assume that V_{nq} is known and we only determine the MM force constants and the reference geometry. This is not a serious restriction, since the parameters of V_{nq} can be determined independently of those of V_q , e.g. by fitting to crystal properties and to *ab-initio* electrostatic potentials (Momany, 1978).

If the *ab-initio* force constant matrix is given in Cartesian coordinates as $(F_{k\alpha, l\beta})$, where k and l run over the atoms and $\alpha, \beta = 1, 2, 3$, the contribution of the nonquadratic interactions can be subtracted from it to yield a new matrix $(F_{k\alpha, l\beta}^q)$ that is purely associated with V_q . Using the chain rule, the second derivatives of V_q with respect to the internal coordinates, i.e. the MM force constants, are then found to be:

$$F_{ij}^{MM} = \sum_{k\alpha} \left[\left(\frac{\partial V_q}{\partial x_{k\alpha}} \right)_{\bar{x}_{\min}} \left(\frac{\partial^2 x_{k\alpha}}{\partial R_i \partial R_j} \right)_{\bar{R}_{\min}} + \sum_{l\beta} \left(\frac{\partial x_{k\alpha}}{\partial R_i} \right)_{\bar{R}_{\min}} \left(\frac{\partial x_{l\beta}}{\partial R_j} \right)_{\bar{R}_{\min}} F_{k\alpha, l\beta}^q \right], \quad (3)$$

where \bar{x}_{\min} and \bar{R}_{\min} denote the minimum of the total potential V in Cartesian and internal coordinates, respectively. In the expression above, the Cartesian gradient of V_q is readily obtained as the negative of the gradient of the nonquadratic interactions since, at the minimum, the total gradient is zero. The first and second derivatives of the Cartesians with respect to the (nonredundant) internal coordinates can be derived from the second derivatives of the internal coordinates with respect to the Cartesians by inversion of a power series (Arfken, 1970) and by requiring that the Cartesian displacement vectors do not represent any translation or rotation of the whole molecule.

To compute the reference geometry we take the derivative of equation (2) with respect to an internal coordinate R_n and equate this to what is obtained for the same derivative using the chain rule, i.e.

$$\sum_j F_{nj}^{MM} (R_j - R_{j0}) = \sum_{k\alpha} \left(\frac{\partial V_q}{\partial x_{k\alpha}} \right)_{\bar{x}_{\min}} \left(\frac{\partial x_{k\alpha}}{\partial R_n} \right)_{\bar{R}_{\min}}, \quad (4)$$

where, for a nonlinear molecule composed of N atoms, the only unknowns are the $3N - 6$ R_{j0} 's. For $n = 1, \dots, 3N - 6$, equation (4) forms a set of $3N - 6$ linear equations which can be solved to yield the reference geometry R_{j0} , $j = 1, \dots, 3N - 6$.

The conversion from *ab-initio* is mathematically exact so that the derived MM energy parameters yield

Table 1. Some examples of calculated MM energy parameters for ethylene corresponding to van der Waals (vdW) interactions of different repulsive strengths*

vdW	$\Delta R_c(\text{\AA})$	$\Delta\alpha$ (degrees)	$F(R_c)$	$F(\alpha)$	$F(\beta)$	$F(\gamma)$
None	0.000	0.0	1347	98	158	36
$\times 1$	0.001	-0.4	1341	97	152	35
$\times 2$	0.005	-2.3	1315	91	127	33
$\times 4$	0.045	-25.7	1214	66	30	21

*The first row corresponds to the original force field (no vdW interactions), vdW $\times 1$ means normal (realistic) vdW interactions, vdW $\times 2$ means that the repulsive parameter has been multiplied by 2, etc. The coordinates referred to are: R_c : C=C bond; α : H-C-H angle; β : in-plane wag; and γ : out-of-plane bend. ΔR_c denotes the deviation of the actual geometry from the reference value, $F(R_c)$ denotes the MM force constant associated with R_c , etc. The units of the force constants are kcal mol⁻¹·Å⁻² for bond stretching, and kcal mol⁻¹·rad⁻² for angle bending.

the same structure and frequencies as the *ab-initio* calculation itself. The conversion procedure also provides a simple means to investigate how different parameters or functional forms of V_{eq} affect the MM force constants and the reference geometry, while the calculated frequencies and structure remain unchanged.

As a simple example the conversion has been applied to ethylene using an empirical valence force field (Pietilä *et al.*, 1986) and nonbonded 1-4 interactions of different repulsive strengths. Some results are given in Table 1. As is seen from the table, the

explicit inclusion of the nonbonded interactions has no large effect on the force constants or the reference geometry, except when the nonbonded interactions are unrealistically strong. This is of course due to the stiff valence coordinates in ethylene. However, in molecules like peptides, the effect of the nonbonded interactions is certainly much more significant. We are presently applying this approach to the conversion of an *ab-initio* force field for peptides (Cheam & Krimm, 1990) to an MM energy function.

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