

Method for the Calculation of the Induced Dipole Moment and the Permanent Multipole-Induced Moment Interaction in Crystals

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Recent work has estimated that for biological molecules [1] and ice [2] induced moments yield $\simeq 25\text{-}30\%$ of permanent-moment-energies. Studies of ice have shown the need for considering large numbers of orientations [3]. Therefore, a method is proposed which offers the following advantages for calculating classical electrostatic interactions in perfect lattices of polarizable species: (A1) Use of a multipole expansion allows decomposition into two stages [4]: *Stage I*. Calculations depending solely on crystal geometry and molecular symmetry. *Stage II*. A very small fraction of the calculations using assumptions about the poorly known quantitative charge distribution which defines multipole moments. This decomposition has the advantage that it has given conclusions independent of the uncertain data of Stage II [3]. (A2) There are variants suitable for 2 types of calculations: *Type A*, a single or a sufficiently small number of orientations of species centred at lattice sites; *Type B*, a larger number of orientations. (A3) There is a convenient error check and the lattice sums converge fairly rapidly.

This work treats the induced dipole term. The induced moment, defined as the difference in the moment of the charge distribution, ρ , in the presence and absence of the field \mathbf{E} , is

$$D_{Ind} = \int \{\rho(\mathbf{X}, \mathbf{E}(\mathbf{X})) - \rho(\mathbf{X}, \mathbf{O})\} \cdot \{\mathbf{X} - \theta\} d\mathbf{X} \quad (1)$$

θ : the origin for the multipole expansion.

Subject to 3 assumptions – (a) ρ is an analytic composite function of \mathbf{X} ; (b) all terms higher than first order in the E_i can be neglected; (c) the variation in $\mathbf{E}(\mathbf{X})$ over the charge distribution can be ignored – the conventional equation,

$$(\mathbf{D}_{Ind} \cdot \mathbf{U}^\gamma) = \alpha_{\gamma\gamma}(\mathbf{E} \cdot \mathbf{U}^\gamma). \quad (2)$$

$\alpha_{\gamma\gamma}$: the element of the polarizability tensor for the principal axis, \mathbf{U}^γ .

can be used to evaluate \mathbf{D}_{Ind} from a small number of parameters which can at least be estimated from experimental data. Since previous studies have shown the importance of higher order permanent multipoles [2, 3], the contribution of all permanent moments to \mathbf{D}_{Ind} have been included, although the induced moments of order $N \geq 2$ have been ignored.

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The equations are stated for the simpler case where symmetry defines the \mathbf{U}^γ since the equations for the general case are essentially the same and merely more complex. The entire lattice of polarizable species can be decomposed into a union of $t = 1, \dots, T$ simple translation lattices for which each lattice site is occupied by an identical molecule or ion. Then the components of \mathbf{D}_{Ind}^t can be obtained from the $3T$ linear equations

$$(\mathbf{D}_{Ind}^{t'} \cdot \mathbf{U}^{\gamma t'}) = \sum_{t=1}^T \left\{ \sum_{\delta=1}^3 C_{\delta t}^{\gamma t'} (\mathbf{D}_{Ind}^t \cdot \mathbf{U}^{\delta t}) \right\} + C^{\gamma t'} \quad (3)$$

$$C_{\delta t}^{\gamma t'} = \alpha_{\gamma\gamma}^{t'} \sum_{t=1}^T \sum'_{\{\mathbf{L}\}} (\mathbf{U}^{\gamma t'} \cdot \nabla_\beta) \|\mathbf{X}_\beta - \mathbf{X}_\alpha\|^{-1} \}_{\mathbf{X}_\beta = \mathbf{O}_{t'}, \mathbf{X}_\alpha = \mathbf{X}_{Lt}}$$

$$C^{\gamma t'} = \alpha_{\gamma\gamma}^{t'} \sum_{t=1}^T \sum_{\{\mathbf{M}_t\}} \sum'_{\{\mathbf{L}\}} (-1)^{m_t+1} \frac{P_{Per}^{M_t}}{m_t!} \prod_{j=1}^{m_t+1} (\mathbf{s}_j^{M_t} \cdot \nabla_\beta) \|\mathbf{X}_\beta - \mathbf{X}_\alpha\|^{-1} \}_{\mathbf{X}_\beta = \mathbf{O}_{t'}, \mathbf{X}_\alpha = \mathbf{X}_{Lt}}$$

∇_β :	grad with respect to \mathbf{X}_β
M_t :	an index for the permanent multipoles of translation lattice, t
m_t :	the order of the permanent multipole, M_t
$\mathbf{S}_j^{M_t}, 1 \leq j \leq m_t$:	characteristic directions of M_t ; $\mathbf{S}_{m_t+1}^{M_t} = \mathbf{U}^{\gamma t'}$
$a_{Per}^{M_t}$:	the scalar permanent multipole moment of M_t
$\sum'_{\{\mathbf{L}\}}$:	a sum over the vectors, \mathbf{L} , for a simple translation lattice (omit $[0, 0, 0]$ when $t = t'$); <i>cf.</i> Equations (3,4,6) of reference [4].

Any, relation such as $\alpha_{\gamma_i \gamma_i}^{t'} = \alpha_{\gamma_j \gamma_j}^{t'}$ reduces the number of independent equations by 1. A convenient method offering advantages (A1-3) has been developed for permanent multipoles [4]. Since the $C_{\delta t}^{\gamma t'}$, $C^{\gamma t'}$ involve the same sort of directional derivatives as those for the permanent multipole lattice calculations, the programme blocks developed for a permanent multipole lattice [4] can be re-used here. Since the previous procedure had advantages (A1-3), the use of these blocks confers the advantages (A1-3) upon the new method for lattices of polarizable species.

Explicit tests with the ice lattice are planned. Then further discussion of the procedure and the results of these tests will be published separately.

References

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