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Relationes

Comments on the Approximate Calculation of Lattice Potential

R. D. Brown and B. W. N. Lo
Department of Chemistry, Monash University, Clayton, Victoria, Australia 3168

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The potential of a charge distribution due to a lattice of point charges may be evaluated by the classical multipole expansion method. The leading terms in the resultant expressions are just those used in some of our previous calculations [1–3]. In addition, for cases where the leading terms vanish because of the effect of orthogonality of the basis functions upon the Mulliken expansion (this being especially serious in the case of a one-centre charge distribution), we have derived the first non-vanishing term, involving $\langle \chi_\mu | r | \chi_\nu \rangle$. In other cases it may be necessary to proceed to still higher multipole terms before a non-zero contribution is obtained. The entire procedure is formulated in such a way that it can be easily applied to LCAO–MO calculations for polyatomic ions in ionic lattices.

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In a series of studies on the effect of ionic lattices on the electronic structures of polyatomic ions [1–3], it is assumed that the contributions of the point-charge lattice to the Hamiltonian of the system under consideration are via the matrix elements of the form

$$\phi_{\mu\nu} = \left\langle \chi_\mu^a \left| \sum_\lambda \frac{Q}{r_\lambda} \right| \chi_\nu^b \right\rangle = \frac{1}{2} S_{\mu\nu} \left\{ \sum_\lambda \frac{Q}{r_{a\lambda}} + \sum_\lambda \frac{Q}{r_{b\lambda}} \right\} \tag{1}$$

where a and b denote the centres of the two atomic orbitals χ_μ and χ_ν respectively, and $S_{\mu\nu}$ is the overlap integral between them. The summation λ is over all point charges Q of the same type throughout the lattice external to the system. $r_{a\lambda}$ represents the distance between a and the lattice point labelled λ. Physically this expression asserts that the interaction between the charge distribution $\varrho_{ab} = \chi_\mu^{a*} \chi_\nu^b$ and the lattice of point charges may be represented by the Madelung potentials at the orbital centres, i.e. the potential of an extended charge distribution ϱ_{ab} has been replaced by that of a point. Therefore we shall refer to Eq. (1) as the *point potential* approximation. It is the purpose of this note to show that this approximation simply represents the leading term in a classical multipole expansion. For the purpose of discussion, it is convenient to differentiate two types of charge distributions.

i) One-Centre Charge Distribution

Here we shall consider ϱ_{aa} arising from two orbitals centred at the same point a, where a set of Cartesian axes is placed. Let r_λ be the position vector of a general lattice point with charge Q, and P an electron with variable position vector $\boldsymbol{r}$ (Fig. 1). The matrix element of Eq. (1) may be written,

$$\phi_{\mu\nu} = Q \sum_\lambda \int G(\boldsymbol{r}_\lambda, \boldsymbol{r})\, \varrho(\boldsymbol{r})\, \mathrm{d}\tau \tag{2}$$

where $G(\boldsymbol{r}_\lambda, \boldsymbol{r}) = \dfrac{1}{|\boldsymbol{r}_\lambda - \boldsymbol{r}|}$ is the familiar Green's function in elementary electrostatics. Here the suffix a is dropped for there is no ambiguity in the choice of origin. If the point charge Q lies completely outside of the charge distribution $\varrho(\boldsymbol{r})$, Eq. (2) may be replaced by a multipole expansion [4, 5]. But this condition is not strictly fulfilled in our case, as $\varrho(\boldsymbol{r})$ is thought to extend over the entire space including the point occupied by Q. However, the majority of the charge density does concentrate at regions close to the origin a, so that we may write Eq. (2) as a Taylor's series about the origin,

$$\begin{aligned}\phi_{\mu\nu} = Q \sum_\lambda \Bigg\{ & G(\boldsymbol{r}_\lambda, 0) \int \varrho(\boldsymbol{r})\, \mathrm{d}\tau + \sum_\alpha \frac{\partial G(\boldsymbol{r}_\lambda, \boldsymbol{r})}{\partial \alpha}\bigg|_{\boldsymbol{r}=0} \int \varrho(\boldsymbol{r})\, \alpha\, \mathrm{d}\tau \\ & + \frac{1}{2!} \sum_{\alpha,\beta} \frac{\partial^2 G(\boldsymbol{r}_\lambda, \boldsymbol{r})}{\partial \alpha\, \partial \beta}\bigg|_{\boldsymbol{r}=0} \int \varrho(\boldsymbol{r})\, \alpha \beta\, \mathrm{d}\tau + \cdots \Bigg\}\end{aligned} \tag{3}$$

α, β etc. $= x, y, z$.

Rearranging the terms, we get

$$\begin{aligned}\phi_{\mu\nu} = Q \Bigg\{ & \langle \chi_\mu | \chi_\nu \rangle \sum_\lambda \frac{1}{r_\lambda} + \langle \chi_\mu | \boldsymbol{r} | \chi_\nu \rangle \cdot \sum_\lambda \frac{\boldsymbol{r}_\lambda}{r_\lambda^3} \\ & + \frac{1}{6} \langle \chi_\mu | 3\boldsymbol{r}\boldsymbol{r} - \boldsymbol{I} r^2 | \chi_\nu \rangle : \sum_\lambda (3\boldsymbol{r}_\lambda \boldsymbol{r}_\lambda - \boldsymbol{I} r_\lambda^2)/r_\lambda^5 + \cdots \Bigg\}\end{aligned} \tag{4}$$

where $\boldsymbol{I}$ is the unit dyadic. Hence $\phi_{\mu\nu}$ is approximated by the interacting potentials of the various multipole moments of $\varrho(\boldsymbol{r})$ and the corresponding derivatives of $G(\boldsymbol{r}_\lambda, \boldsymbol{r})$. The first term in (4) is just the point potential approximation used in [2].

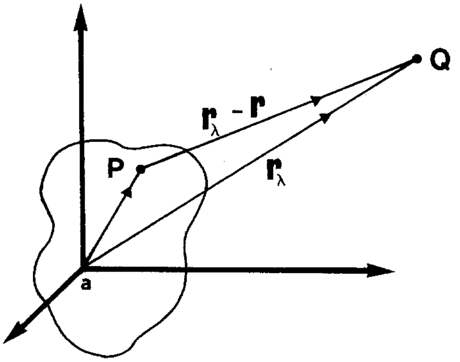

Fig. 1. Interaction between the point charge Q and a one-centre charge distribution ϱ_{aa}

ii) Two-Centre Charge Distribution

To arrive at the type of expression used in [2, 3], the two-centre charge distribution ϱ_{ab} is first approximated by the sum of two one-centre charge distributions using the Mulliken method [6], and then the same type of derivation as above is applied:

$$\begin{aligned}\phi_{\mu\nu} = \frac{1}{2} S_{\mu\nu} Q \sum_{\lambda} \Bigg\{ & \left[\frac{1}{r_{a\lambda}} + \frac{1}{r_{b\lambda}}\right] + \left[\langle \chi_{\mu}^{a} | \boldsymbol{r}_{a} | \chi_{\mu}^{a} \rangle \cdot \frac{\boldsymbol{r}_{a\lambda}}{r_{a\lambda}^{3}} \right. \\ & \left. + \langle \chi_{\nu}^{b} | \boldsymbol{r}_{b} | \chi_{\nu}^{b} \rangle \cdot \frac{\boldsymbol{r}_{b\lambda}}{r_{b\lambda}^{3}} \right] + \frac{1}{6} \left[\langle \chi_{\mu}^{a} | 3\boldsymbol{r}_{a}\boldsymbol{r}_{a} - \boldsymbol{I} r_{a}^{2} | \chi_{\mu}^{a} \rangle : \left(\frac{3\boldsymbol{r}_{a\lambda}\boldsymbol{r}_{a\lambda} - \boldsymbol{I} r_{a\lambda}^{2}}{r_{a\lambda}^{5}} \right) \right. \\ & \left. + \langle \chi_{\nu}^{b} | 3\boldsymbol{r}_{b}\boldsymbol{r}_{b} - \boldsymbol{I} r_{b}^{2} | \chi_{\nu}^{b} \rangle : \left(\frac{3\boldsymbol{r}_{b\lambda}\boldsymbol{r}_{b\lambda} - r_{b\lambda}^{2}\boldsymbol{I}}{r_{b\lambda}^{5}} \right) \right] + \cdots \Bigg\}\end{aligned} \tag{5}$$

where $\boldsymbol{r}_{ax}$ and $\boldsymbol{r}_{bx}$ ($x = \langle\text{empty}\rangle$ or λ) are vectors referring to centres a and b as origin respectively, and where we have assumed that the basis atomic orbitals are normalized. The first square bracket is just the point potential approximation used in [2, 3].

A similar expression may be obtained if Ruedenberg's approximation is used for the two-centre charge distribution; however we prefer to take a different approach. The charge distribution ϱ_{ab} is expanded as a point multipole about the midpoint c of the two orbital centres a and b. Following similar arguments, we have

$$\begin{aligned}\phi_{\mu\nu} = Q \sum_{\lambda} \Bigg\{ & \langle \chi_{\mu}^{a} | \chi_{\nu}^{b} \rangle \frac{1}{r_{c\lambda}} + \langle \chi_{\mu}^{a} | \boldsymbol{r}_{c} | \chi_{\nu}^{b} \rangle \cdot \frac{\boldsymbol{r}_{c\lambda}}{r_{c\lambda}^{3}} \\ & + \frac{1}{6} \langle \chi_{\mu}^{a} | 3\boldsymbol{r}_{c}\boldsymbol{r}_{c} - \boldsymbol{I} r_{c}^{2} | \chi_{\nu}^{b} \rangle : \frac{3\boldsymbol{r}_{c\lambda}\boldsymbol{r}_{c\lambda} - \boldsymbol{I} r_{c\lambda}^{2}}{r_{c\lambda}^{5}} + \cdots \Bigg\}\end{aligned} \tag{6}$$

where c is now chosen as the origin of the vectors $\boldsymbol{r}_{c}$ and $\boldsymbol{r}_{c\lambda}$ etc.

From the preceding discussion, it is clear that the point potential approximation employed in [1–3] does give a reasonable estimate of the lattice contribution, but may lead to erroneous values if the leading term in (4) or (5) vanishes because of $\langle \chi_{\mu} | \chi_{\nu} \rangle = 0$ (by virtue of the orbital symmetry or otherwise). In such cases the next higher non-vanishing term should be used.

If the full Eq. (4) and (6) are used, only a few terms need be calculated because these expressions converge rapidly. When the lattice potential is calculated in this manner, it will be referred to as the multipole potential approximation. The validity of this approximation depends on the extent to which the condition of non-overlapping of ϱ_{ab} and Q has been fulfilled. It should be pointed out that this method is equivalent to the common practice in crystal field calculations, where the function $G(\boldsymbol{r}_{\lambda}, \boldsymbol{r})$ is first replaced by a harmonic polynomial before integration [7]. Here we have formulated the procedure in such a way that it is easily applicable to LCAO–MO calculations. Eq. (4) and (6) as they stand are quite general and may be used for different types of atomic functions, (e.g. Gaussian or exponential). A more accurate approach has been developed for charge distributions arising from products of STO's [8].

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Professor R. D. Brown
Department of Chemistry
Monash University
Clayton, Victoria, Australia 3168