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Approximate Electric Potentials

George G. Hall

Department of Mathematics, University, Nottingham NG7 2RD, UK

It is shown that the electrostatic energy functional is the only one available for fitting a given potential using approximate electric potentials arising from point charges. The significance of this fitting is examined in terms of splines. To illustrate the method the electron densities of atoms are modelled using point charges at the vertices of tetrahedra and of cubes.

Key words: Point charge approximations – Electric potentials in atoms – Self-energy.

1. Introduction

The electrostatic potential around an atom or molecule is a major factor in determining the interaction energy between it and other molecules. Calculations on condensed phases become feasible only if this energy can be estimated with speed and accuracy. This paper is concerned with point charge models since these can be very efficient in practice and very easy to visualise. The assumption is made that the purpose of the model is to describe the potential as well as possible. It is then shown, using ideas from the theory of splines, that the Dirichlet functional, which gives the total energy of a charge distribution, is the only satisfactory criterion for the fitting. The self-energy of the point charge, which is a problem for classical electrostatics, is avoided by a simple device.

The theory is applied to the H, He, Li and Be atoms using tetrahedral and cubical arrays of charges. These demonstrate that the charges give a potential which is of high accuracy for relatively large distances and still tolerable for short distances. The use of these charges to calculate other properties is also illustrated.

2. The Optimizing Functional

If the potential at the point $\boldsymbol{r}$ is $\phi(\boldsymbol{r})$ and $\phi^*(\boldsymbol{r})$ is an approximation to it then any functional used to determine an optimal fitting must depend on the error potential $(\phi - \phi^*)$. The simplest such functional is the least squares one

$$\int (\phi - \phi^*)^2 \, d\tau. \tag{1}$$

When ϕ^* is derived from a point charge of magnitude q_t at the position $\boldsymbol{r}_t$ then

$$\phi^* = q_t / |\boldsymbol{r} - \boldsymbol{r}_t| \tag{2}$$

and the integral $\int (\phi^*)^2 \, d\tau$ diverges over the infinite volume. Thus (1) cannot be used as the functional.

In the theory of splines [1] the fitting of one function to another can be achieved by minimizing a functional whose integrand is the square of the difference in some higher derivative. The cubic spline, for example, involves the difference of second derivatives. There are several ways in which the spline idea can be generalized to $\mathbb{R}^3$. For the present purpose the dissection of space into volumes, within which the function is a polynomial, is not useful but the idea of optimizing a functional, with certain points, or nodes, selected for close fitting, is still valuable. In three dimensions it is necessary to insist that the form of the functional should be invariant to rotations of space. An appropriate functional using the second derivatives would then be

$$\int (\nabla^2 \phi - \nabla^2 \phi^*)^2 \, d\tau \tag{3}$$

since the Laplacian operator is invariant to coordinate rotations. Because of the Poisson equation this is equivalent to a least squares fitting of the electron density. The functional (3) also leads to difficulties. Under suitable boundary conditions involving ϕ becoming small at large distances, (3) can be transformed into

$$\int (\phi - \phi^*)(\nabla^4 \phi - \nabla^4 \phi^*) \, d\tau, \tag{4}$$

just as the cubic spline is generated by expressing the fourth derivative as a sum of delta functions, so $\nabla^4 \phi^*$ is taken as a linear combination of three-dimensional delta functions. The solution to

$$\nabla^4 \phi^* = -4\pi q \delta(\boldsymbol{r} - \boldsymbol{r}_t) \tag{5}$$

is

$$\nabla^2 \phi^* = q / |\boldsymbol{r} - \boldsymbol{r}_t|$$

and hence

$$\phi^* = \tfrac{1}{2} q |\boldsymbol{r} - \boldsymbol{r}_t|. \tag{6}$$

This means that ϕ^* is itself divergent for large r and the functional is even more so.

The Dirichlet functional of the error field,

$$U = \frac{1}{8\pi} \int (\nabla\phi - \nabla\phi^*)^2 \, d\tau \tag{7}$$

is intermediate between the others and, since it has the physical significance of being an energy, has more reason to be finite. It is equivalent to a least squares fit of the electric fields. It transforms into

$$-\frac{1}{8\pi} \int (\phi - \phi^*)(\nabla^2\phi - \nabla^2\phi^*) \, d\tau \tag{8}$$

and $\nabla^2\phi^*$ can be represented as a sum of delta functions without any immediate difficulty. There is a long history of using the Dirichlet functional in solving electrostatic problems [2]. By definition $U \geq 0$ and its magnitude measures the quality of the approximation. The use of this functional for continuous charge distributions ρ^* is discussed elsewhere [3].

3. Point Charges

Every classical theory involving point charges has difficulties over the self-energy of the charge if it remains a point charge. These can be avoided by giving the charge a small spherical shape. It is simplest to treat this as a conducting ball so that all the charge resides on the surface and the potential inside is uniform but it could also be treated as a solid ball of charge. Because of the spherical shape the potential outside retains the point charge form provided the balls never overlap. The self-energy of a point charge of magnitude q when spread over a sphere of radius a is

$$\tfrac{1}{2}q^2/a. \tag{9}$$

The electron density is modelled by a set of point charges

$$\rho^*(\boldsymbol{r}) = \sum_t q_t \delta(\boldsymbol{r} - \boldsymbol{r}_t) \tag{10}$$

where q_t is the charge at $\boldsymbol{r}_t$. The corresponding potential is

$$\phi^*(\boldsymbol{r}) = \sum_t q_t / |\boldsymbol{r} - \boldsymbol{r}_t|. \tag{11}$$

The functional U becomes

$$\begin{aligned} U &= \frac{1}{2} \int (\phi - \phi^*)(\rho - \rho^*) \, d\tau \\ &= \frac{1}{2} \int \phi\rho \, d\tau - \int \phi\rho^* \, d\tau + \frac{1}{2} \int \phi^*\rho^* \, d\tau. \end{aligned} \tag{12}$$

The first term is the energy of the original distribution. The second becomes

$$\int \phi\rho^* \, d\tau = \sum_t q_t\phi_t \tag{13}$$

where $\phi_t = \phi(\boldsymbol{r}_t)$. Strictly, when the point becomes a ball, the potential averaged over the spherical surface is required. By expanding ϕ around the centre of the sphere it can be shown that

$$\int \phi\rho^* \, d\tau = \sum_t q_t(\phi_t - 2\pi a_t^2\rho_t) + \mathrm{O}(a_t^4) \tag{14}$$

where a_t is the radius of the sphere and $\rho_t = \rho(\boldsymbol{r}_t)$. Since a_t is assumed to be small, this extra term in (14) is a small correction and will be ignored. The final term is

$$\frac{1}{2}\int \phi^*\rho^* \, d\tau = \frac{1}{2}\sum_{s\neq t}\sum q_sq_t/r_{st} + \frac{1}{2}\sum_s q_s^2/a_s \tag{15}$$

where $r_{st} = |\boldsymbol{r}_s - \boldsymbol{r}_t|$. The influence of the self-energy term can be greatly reduced by assigning radii proportional to the square of the charges

$$a_s = q_s^2/(2b) \tag{16}$$

so that each has the same self-energy, b, and the term becomes a fixed constant. Thus, for N charges,

$$U = \frac{1}{2}\int \phi\rho \, d\tau - \sum_t q_t\phi_t + \frac{1}{2}\sum_{s\neq t}\sum q_sq_t/r_{st} + Nb, \tag{17}$$

where (13) is used instead of (14).

The optimum value of q_t is found by differentiation of (17)

$$\frac{\partial U}{\partial q_t} = -\phi_t + \sum_{s\neq t} q_s/r_{st} = 0. \tag{18}$$

This can be interpreted as determining the charges so that the approximate potential at each charge is equal to the true potential there. The optimized value of U is

$$U_{\text{opt}} = \frac{1}{2}\int \phi\rho \, d\tau - \frac{1}{2}\sum_{s\neq t} q_sq_t/r_{st} + Nb. \tag{19}$$

Similarly the location of the charges is found by taking the gradient of (17).

$$\frac{\partial U}{\partial \boldsymbol{r}_t} = -q_t\frac{\partial \phi_t}{\partial \boldsymbol{r}_t} + q_t\sum_{s\neq t} q_s\frac{\partial}{\partial \boldsymbol{r}_t}\left(\frac{1}{r_{st}}\right) = 0. \tag{20}$$

which equates the electric fields

$$\boldsymbol{E}_t = \boldsymbol{E}_t^*. \tag{21}$$

Thus, as in spline theory, the optimization of the functional ensures that the potential and its gradient are exactly fitted at the point charge positions.

4. Modified Point Charges

In many applications the approximate potential will be used at large rather than small distances from the nuclei and consequently some modification of the procedure to ensure accurate long-range behaviour is desirable. The easiest constraint to impose is that the total charge should be conserved since this produces the correct first term in the asymptotic potential. The constraint is introduced by means of a Lagrange multiplier and the functional to be optimized becomes

$$W = U - \lambda \sum_t q_t. \tag{22}$$

In this treatment it is appropriate to adopt an assignment of the radii, which replaces (16),

$$a_s = q_s/(2c) \tag{23}$$

so that each sphere is at the same potential and

$$\frac{1}{2}\sum_s q_s^2/a_s = c \sum_s q_s. \tag{24}$$

Thus

$$W = \frac{1}{2}\int \phi\rho \, d\tau - \sum_t q_t\phi_t + \frac{1}{2}\sum_{s\neq t}\sum q_t/r_{st} + (c-\lambda)\sum_t q_t. \tag{25}$$

The optimum charges now satisfy

$$\frac{\partial W}{\partial q_t} = -\phi_t + (c-\lambda) + \sum_{s\neq t} q_s/r_{st} = 0 \tag{26}$$

instead of (18) so that the approximate potential at each point charge now differs from the true potential by the constant amount $(c-\lambda)$. On the other hand the optimization of the locations forces the electric fields at the points to agree since (20) remains the equations determining them. The optimized value of W, when (26) is satisfied, is

$$W_{\text{opt}} = \frac{1}{2}\int \phi\rho \, d\tau - \frac{1}{2}\sum_{s\neq t}\sum q_s q_t/r_{st} \tag{27}$$

and this is exactly the classical expression with no self-energy. The multiplier λ is a parameter in Eqs. (26) and is determined by fixing the total charge

$$\sum_t q_t = Q. \tag{28}$$

It is satisfactory to note that c can be absorbed into λ and eliminated from (27). Because of the constraint term, W is not necessarily positive but its magnitude remains a useful global measure of the fitting. This use of W corresponds to Thomson's theorem rather than Dirichlet's theorem in the classical context [2].

5. Tetrahedra

To illustrate the power and utility of these ideas it is interesting to apply them to atoms since the spherical charge density is very different from a set of point charges. Some symmetry can be retained by restricting the points to be the vertices of a regular solid. The simplest is the tetrahedron.

The results of a fitting of 4 charges in tetrahedral configuration are shown in Table 1. The electron densities calculated from Hartree–Fock wavefunctions were used [4].

Since the charges are fixed, only the radius of the tetrahedron R is optimized. As might be expected, the values of W_{opt} show that the quality of the fitting deteriorates rapidly as the total charge increases. The two last rows show the mean value of $1/r$ compared with the point approximation Q/R. The approximation is 20–30% higher.

6. Cubes

The next simplest regular solid is the cube. Each point charge is $\frac{1}{8}$ of the total charge and only the radius is optimized. The results are summarized in Table 2. They show a pattern very similar to those for tetrahedra but the accuracy, as judged by the value of W_{opt} and by the closeness of Q/R to mean value of $1/r$, is substantially improved.

One way of extending these calculations is to surround the cube by a second conformal cube. The charges on each are found by solving the linear equations (26). The equations for the cube radii (20) are non-linear so these radii are determined by direct minimization of W_{opt}. When this optimization was applied

Table 1. Charge tetrahedra

	H	He	Li	Be
R	0.7621	0.4918	0.3807	0.3458
$\frac{1}{2}\int \rho\phi\, d\tau$	0.3125	2.0515	4.0621	7.1561
W_{opt}	0.0112	0.1837	−1.3673	−3.4702
$\int \rho/r\, d\tau$	1	3.3746	5.7154	8.4088
Q/R	1.3121	4.0668	7.8810	11.5684

Table 2. Charge cubes

	H	He	Li	Be
R	0.9042	0.6043	0.5274	0.4792
$\frac{1}{2}\int \rho\phi\, d\tau$	0.3125	2.0515	4.0621	7.1561
W_{opt}	−0.0286	0.0098	−1.2017	−3.1433
$\int \rho/r\, d\tau$	1	3.3746	5.7154	8.4088
Q/R	1.1060	2.4069	3.5530	8.3477

to the atoms on a computer it proved to be very unstable with various local minima. Only for Be were the results consistent and reproducible.

The inner cube for Be had a radius of 0.3458 and each charge was 0.3662. The outer cube had radius 2.8011 and charges of 0.1338. The value of W_{opt} is reduced to 1.7445. The mean value of $1/r$ for the charges is 8.8539.

For Li there seemed to be convergence towards a minimum which had radii 0.4297, 4.6564 and charges 0.3361, 0.03894. This gives $W_{\text{opt}} = 1.3125$ and a mean $1/r$ of 6.3235.

7. Potential Fitting

Since the purpose of the optimization is to fit the electrostatic potential it is of interest to compare them directly. For H the potential is exactly

$$\phi = (1 - e^{-2r}(1 + r))/r \tag{29}$$

so this atom is convenient to use to illustrate the results. Very similar results are found for other atoms. Table 3 shows ϕ and the approximate potential ϕ^* due to the point charges for selected values of r. The asymptotic form, $1/r$, is included for comparison. The point charge potential is not spherically symmetric so a direction has to be selected. The middle of a tetrahedron edge has been chosen since this is a minimum path for ϕ^* and so the comparison is more meaningful.

This table shows clearly that the approximate potentials reproduce the $1/r$ behaviour at large distances as they are constrained to do and that they tend to a realistic finite value near the nucleus. Thus a cluster of four charges is sufficient to demonstrate the pentration effect when the field point is inside the charge cloud. The improvement on increasing to eight charges is most apparent in this inner penetration zone.

8. Conclusion

It has been shown that the electrostatic energy of the error field is a functional which can be minimized, subject to the constraint of a constant total charge,

Table 3. Electrostatic potential for H atom

r	ϕ	ϕ^* (tetrahedron)	ϕ^* (cube)	$1/r$
0.0885	0.9952	1.3110	1.1059	11.2951
0.2656	0.9637	1.2869	1.1029	3.7650
0.6197	0.8569	1.1112	1.0392	1.6136
1.3280	0.6299	0.7000	0.7085	0.7530
2.7446	0.3587	0.3606	0.3628	0.3644
5.5777	0.1793	0.1790	0.1792	0.1793
11.2438	0.08894	0.08892	0.08894	0.08894

using point charges to represent the electron distribution. Since this is a fitting of the electrostatic potential it is not surprising that the approximate potentials reproduce fairly closely the true ones. It is pleasing to see that problems over the self-energy of the point charge can be eliminated. Other energy-related quantities can be estimated from the point charges. The electrostatic energy itself is tolerably approximated for the smaller atoms but becomes poor as the individual point charges increase. The electron-nuclear energy behaves similarly.

A by-product of these calculations has been the realization that when more than one point charge is used to represent the electrons in an atom the charges must not coincide with the nucleus. For the electric potential the penetration effect, the finite potential at the nucleus, is second only to the correct asymptotic form. When point charges are used to represent the electron density in molecules it follows that the penetration effect at one atom will be affecting the charges used for its neighbours.

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