

"Some Relationships Between Different Uses of the Electrostatic Potential," D. G. Truhlar, in Chemical Applications of Atomic and Molecular Electrostatic Potentials, edited by P. Politzer and D. G. Truhlar (Plenum Press, New York, 1981), pp. 85-91.

doi.org/10.1007/978-1-4757-9634-6_6

SOME RELATIONSHIPS BETWEEN DIFFERENT USES OF
THE ELECTROSTATIC POTENTIAL

Donald G. Truhlar

Department of Chemistry and Chemical Physics Program
University of Minnesota
Minneapolis, MN 55455.

The electrostatic potential at a point \vec{r} in the vicinity of an atom or molecule is (in a.u.):

$$v^{ES}(\vec{r}) = \sum_A \frac{Z_A}{|\vec{r} - \vec{R}_A|} - \int \frac{\rho(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' \quad (1)$$

where Z_A is the charge on nucleus A, located at \vec{R}_A , and $\rho(\vec{r}')$ is the electronic charge density. As is clear from equation (1), the electrostatic potential represents the net electric potential field at point \vec{r} caused by the unperturbed, *i.e.*, static, charge distribution of an atom or molecule. As such the electrostatic potential determines the classical coulombic component of the interaction energy of a static target with anything. In this chapter a few relationships and differences between various kinds of uses of the electrostatic potential are discussed.

The electrostatic potential plays an important role in density functional theories. At their most sophisticated, density functional theories attempt to utilize the theorem¹ that the exact quantum mechanical energy of a system of charged particles is a functional of the charge density. So far, however, a practical operational formula for the exact functional is unknown and the theorem just quoted serves mainly as a stimulus to further work and as a justification in principle for applying and testing approximate functionals based on physical models. The simplest example of a density-functional theory is Thomas-Fermi theory.² In Thomas-Fermi theory one uses the free-electron-gas model to obtain a kinetic energy functional, and the potential energy is approximated as the coulomb

energy, which is calculated from the electrostatic potential and the density. In Thomas-Fermi-Dirac theory^{2,3} one augments the kinetic-energy and coulomb-energy terms with an exchange-energy functional, which is also obtained from the free-electron-gas model. In the Thomas-Fermi and Thomas-Fermi-Dirac theories, the electron density is obtained variationally from the energy functional. For molecular problems, however, more accurate results can be obtained by using more accurate electron densities. The Gordon-Kim method⁴ is one method for incorporating more accurate electron densities in a density functional context. In this method the electron density of an interacting system is obtained by adding accurate (Hartree-Fock or better) densities for the two interacting units; additivity is assumed to hold even in the region where the subsystem densities overlap. In addition, the Thomas-Fermi-Dirac energy functional is augmented by a correlation-energy functional. Because of the additivity assumption the Gordon-Kim method is restricted to cases where at least one of the interacting units is a closed-shell species. In the Gordon-Kim method the coulombic energy for the interaction of units A and B may be written

$$E_{\text{coul}} = E_{\text{nn}} + E_{\text{en}} + E_{\text{ee}} \quad (2)$$

where the individual components contain the nucleus-nucleus, nucleus-electron, and electron-electron terms, respectively. The latter two components can be written as

$$E_{\text{en}} = - \sum_{\alpha} Z_{\alpha} V_{\text{B}}^{\text{ES}}(\vec{r}_{\alpha}) - \sum_{\beta} Z_{\beta} V_{\text{A}}^{\text{ES}}(\vec{r}_{\beta}) \quad (3)$$

and

$$E_{\text{ee}} = \int \rho_{\text{A}}(\vec{r}) V_{\text{B}}^{\text{ES}}(\vec{r}) d\vec{r} \quad (4a)$$

$$= \int \rho_{\text{B}}(\vec{r}) V_{\text{A}}^{\text{ES}}(\vec{r}) d\vec{r} \quad (4b)$$

where α and β denote the nuclei of A and B, respectively, \vec{r}_{α} and \vec{r}_{β} denote the nuclear positions, $\rho_{\text{A}}(\vec{r})$ and $\rho_{\text{B}}(\vec{r})$ denote the electronic densities, and $V_{\text{A}}^{\text{ES}}(\vec{r})$ and $V_{\text{B}}^{\text{ES}}(\vec{r})$ denote the electrostatic potentials. These equations illustrate the strong involvement of the electrostatic potential in the Gordon-Kim method, which has proved successful for calculating interaction energies in many cases.⁵

Often one can use the electrostatic potential alone, *i.e.*, without calculating the full energy functional or even the full coulombic interaction energy, to gain some insight into the total interaction energy and its dependence on direction of approach of the subsystems or interaction site. Since the electrostatic

potential is a functional of the unperturbed density of a single interaction partner, it is expected to be most useful for cases where the interaction does not involve large changes in the electron density. Good examples are cases where one or both collision partners have closed-shell structures and both are neutral. Such cases are considered in detail in several of the chapters of this book, for example, the chapter by Kollman on non-covalent complexes. However, the restriction to this kind of system is too conservative, and the electrostatic potential has actually been found to be useful for understanding structure and reactivity in a broader context, *e.g.*, in cases involving ions even when ion-induced-dipole forces and/or covalent-bond forces also play important roles. Although it is clear that one must be careful not to rely heavily on the electrostatic potential in cases where the classical coulombic interaction of the unpolarized charge distributions is not the dominant interaction, the use of the electrostatic potential as a tool to correlate structure and reactivity in a wide variety of cases is now well established.^{6,7}

One can test the success of interpretations of interaction energy that are based on the electrostatic potential or the Gordon-Kim method in two ways. First, one can compare to experiment and judge the success of theoretical models strictly empirically. This is often the only possible method, and there have been many successful applications of electrostatic potential models to explain, correlate, or predict experimental observables with good success. In favorable cases one can test the electrostatic potential models by performing a better calculation. For these tests the interaction energy can be calculated exactly rather than approximated by coulombic energy alone or by a functional of density. Also the wave function for the interacting system can be determined by molecular orbital theory or by the configuration-interaction method. Having done a better calculation of the interaction energy, one can examine the details of the better calculation to understand the roles of various quantities, *e.g.*, the coulombic energy calculated from the electrostatic potential; in this way one can better justify methods based on coulombic energy and also learn their limitations. Techniques for such energy-component analyses have been developed by Morokuma and coworkers.⁸

Equation (1) shows that the electrostatic potential is directly calculable from the electron density and in fact the electrostatic potential function $V^{ES}(\vec{r})$ and the electron density function $\rho(\vec{r})$ contain equivalent information. The electrostatic potentials used for the applications discussed above^{6,7} were all obtained from quantum mechanical calculations of the electron density. It would be useful to be able to obtain accurate values of $V^{ES}(\vec{r})$ or $\rho(\vec{r})$ directly from experiment to obviate these quantum mechanical calculations or to test their accuracy. As discussed next, information

about $\rho(\vec{r})$ is obtained most directly from scattering experiments where the molecule interacts with photons or electrons rather than other molecules.

We have already mentioned that the molecular electrostatic potential is the coulombic potential energy that a positive point charge would experience at a given position in the presence of a molecule. Electrostatic potentials occur in the theoretical treatment of both electron-molecule interactions and molecule-molecule interactions. However, there is an important difference in the way they enter in these two cases. Consider first molecule-molecule interactions. These are usually treated using the Born-Oppenheimer separation⁹ of electronic and internuclear motion. This means that the electronic charge distributions should adjust adiabatically and completely to the instantaneous geometry of the nuclear framework; the energy of the relaxed charge distribution provides the Born-Oppenheimer potential energy surface as a function of internuclear coordinates. A favorable interaction between two reactants, such as an interaction leading to binding or an exothermic reaction, might be expected to occur if the geometry corresponds to a nucleophilic site on one reagent, say A, being in a position of negative electrostatic potential for the other reagent, say B. Alternatively, it would be favorable to have an electrophilic site of A in a position of positive electrostatic potential of B. Thus the electrostatic potential of B can serve to correlate its reactivity toward many possible reagents. Of course for more quantitative and definitive predictions about the reactivity of B toward some specific A, one should calculate the full potential energy hypersurface for the A-B supersystem as a function of all relevant geometric parameters. One should also add solvent interactions if they are present and non-negligible. This procedure is often impractical, and anyway it lacks the generality of correlating reactivity with a fundamental and general property of the isolated molecule B. Thus it is for convenience rather than lack of a more rigorous framework that correlations of reactivity with electrostatic potential are of great interest. The connection between the molecular electrostatic potential and the true potential energy of interaction is discussed in more detail in the chapter by Morokuma and Kitaura in this book.

At very high energies, the Born-Oppenheimer approach breaks down. For example, in a collision of C^+ with H, the relative speed of the nuclei becomes equal to the speed of the electron in the first Bohr orbit of H at a center-of-mass translational energy of 23 keV. At such an energy the assumption that the electronic charge distribution adiabatically follows the nuclear motion would be very bad, and the electrostatic potential based on the unperturbed charge distribution would be a more nearly correct description of the actual effective potential. Of course this energy is much higher than those encountered in the chemical regime so the electrostatic

potential as a correlant of chemical reactivity must be justified by a more indirect argument as discussed above. For electron scattering, however, the relative speed of projectile and target is the same as the speed of an electron in the first Bohr orbit of H at an impact energy of 13.6 eV. Since we are often interested in impact energies this high or even much higher, the electrostatic potential is a much more valid physical approximation to the true effective potential for electron scattering than for molecule-molecule interactions. There is another important difference between molecule-molecule interactions and electron-molecule scattering. For the former, the general validity of the Born-Oppenheimer approximation means that the true effective potential, to an excellent approximation, is local and independent of translational energy. For electron scattering the true effective potential is both very nonlocal and significantly energy dependent. Even for very low-energy electron scattering, the incident electron is speeded up by the attractive nuclear field and the adiabatic approximation is not valid in the strong interaction region. At very high energy, however, things simplify. At very high impact energy, exchange of target and incident electrons may be neglected, and target charge polarization may also be neglected. Then the scattering is controlled by the same electrostatic potential as defined above. Furthermore, at very high energy the scattering event may be treated by first order perturbation theory, *i.e.*, the first Born approximation.¹⁰ In this case it is possible to extract the target charge density (and hence the electrostatic potential) directly from the experiment. In practice such inversion is usually carried out only for impact energies in the electron diffraction energy range, 20-50 keV. Such experiments may be considered to be the direct experimental measurement of the electrostatic potential. The target charge density is also measurable by X-ray diffraction. The lower-energy electron scattering regime where both the electrostatic potential and its corrections play important roles is discussed in my later chapter in this book.

It is instructive to compare X-ray diffraction and electron diffraction in more detail. X-ray diffraction directly explores the electron density because it is the electrons that scatter the photons. In contrast, for electron scattering it is electric potential which is important. At high enough electron impact energy, the electric potential is well approximated by the electrostatic potential. Thus X-ray diffraction and high-energy electron scattering, *i.e.*, electron diffraction, yield equivalent information, but the former is more naturally interpreted in terms of electron density and the latter in terms of electrostatic potential.

So far we have emphasized interaction energies. Interaction energies are total energies for composite systems minus total energies for separated systems. Therefore, one approach to

interaction energies is to calculate these total energies. Since electrostatic potentials for interacting systems can be calculated more accurately than total energies can, it would be a very important quantitative advance if we could express the total energy of a system in terms of the electrostatic potential for the system. We have already mentioned the strong connection between the electron density and the electrostatic potential. Thus writing the total energy as a functional of electrostatic potential is equivalent to writing it as a functional of electron density, and this brings us back to the very fundamental density functional theories that provided a starting point for this chapter.

In summary, we have discussed how the electrostatic potential arises naturally in several theoretical contexts. We have also discussed how the motivation and justification and the role it plays are sometimes quite different in these different contexts.

REFERENCES

1. P. Hohenberg and W. Kohn, Inhomogeneous electron gas, *Phys. Rev.* 136:B864 (1964). See also R. G. Parr, R. A. Donnelly, M. Levy and W. E. Palke, Electronegativity: the density functional viewpoint, *J. Chem. Phys.* 68:3801 (1978).
2. See, *e.g.*, P. Gombás, "Die Statistische Theorie des Atoms und ihre Anwendungen," Springer, Vienna (1949); P. Gombás, Statische Behandlung des Atoms, in: "Handbuch der Physik," S. Flügge, ed., Springer-Verlag, Berlin (1956), Vol. 36, p. 109; N. H. March, The Thomas-Fermi approximation in quantum mechanics, *Advan. Phys.* 6:1 (1957); E. H. Lieb and B. Simon, The Thomas-Fermi theory of atoms, molecules, and solids, *Advan. Math.* 23:22 (1977).
3. P. A. M. Dirac, Note on exchange phenomena in the Thomas-atom, *Proc. Cambridge Phil. Soc.* 26:376 (1930).
4. R. G. Gordon and Y. S. Kim, Theory for the forces between closed-shell atoms and molecules, *J. Chem. Phys.* 56:3122 (1972).
5. For a review see M. J. Clugston, The calculation of intermolecular forces. A critical examination of the Gordon-Kim method, *Advan. Phys.* 27:893 (1978).
6. E. Scrocco and J. Tomasi, The electrostatic molecular potential as a tool for the interpretation of molecular properties, *Top. Curr. Chem.* 42:95 (1973); E. Scrocco and J. Tomasi, Electronic molecular structure, reactivity, and intermolecular forces: an heuristic interpretation by means of electrostatic molecular potentials, *Advan. Quantum Chem.* 11:116 (1978); J. Tomasi, On the use of electrostatic molecular potentials in theoretical investigations on chemical reactivity, in: "Quantum Theory of Chemical Reactions," R. Daudel, A. Pullman,

- L. Salem and A. Veillard, eds., D. Reidel Publishing Co., Dordrecht, Holland (1979), Vol. I, p. 191.
7. P. Politzer and K. C. Daiker, Models for chemical reactivity, in: "The Force Constant in Chemistry," D. M. Deb, ed., Van-Nostrand-Reinhold, Princeton, NJ (1980), in press.
 8. K. Morokuma, Molecular orbital studies of hydrogen bonds. III. C=O...H-O hydrogen bond in $\text{H}_2\text{CO}\cdots\text{H}_2\text{O}$ and $\text{H}_2\text{CO}\cdots 2\text{H}_2\text{O}$, J. Chem. Phys. 55:1236 (1971); K. Kitaura and M. Morokuma, A new energy decomposition scheme for molecular interactions within the Hartree-Fock approximation, Int. J. Quantum Chem. 10:325 (1976).
 9. See, *e.g.*, A. Messiah, "Quantum Mechanics," North-Holland, Amsterdam (1963), Vol. II, pp. 781-793; or P. R. Bunker, "Molecular Symmetry and Spectroscopy," Academic, New York (1979), pp. 166-168.
 10. M. Fink and C. Schmiedekamp, Precise determination of differential electron scattering cross sections. III. Exchange corrections (CH_4 , N_2 , CO_2 , and Kr), J. Chem. Phys. 71:5243 (1979).