SOME RELATIONSHIPS BETWEEN DIFFERENT USES OF
THE ELECTROSTATIC POTENTIAL

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

\[
V_{\text{ES}}(\mathbf{r}) = \sum_{A} \frac{Z_{A}}{|\mathbf{r} - \mathbf{R}_{A}|} - \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'
\]  

(1)

where \( Z_{A} \) is the charge on nucleus \( A \), located at \( \mathbf{R}_{A} \), and \( \rho(\mathbf{r}') \) is the electronic charge density. As is clear from equation (1), the electrostatic potential represents the net electric potential field at point \( \mathbf{r} \) 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 theorem\(^1\) 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\textsuperscript{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 method\textsuperscript{4}
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

\begin{equation}
E_{\text{coul}} = E_{\text{nn}} + E_{\text{en}} + E_{\text{ee}}
\end{equation}

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

\begin{equation}
E_{\text{en}} = -\sum_{\alpha} z_{\alpha} v_{\text{ES}}(\mathbf{r}_{\alpha}) - \sum_{\beta} z_{\beta} v_{\text{ES}}(\mathbf{r}_{\beta})
\end{equation}

and

\begin{align}
E_{\text{ee}} &= \int \rho_{A}(\mathbf{r}) v_{\text{ES}}(\mathbf{r}) d\mathbf{r} \\
&= \int \rho_{B}(\mathbf{r}) v_{\text{ES}}(\mathbf{r}) d\mathbf{r}
\end{align}

where \(\alpha\) and \(\beta\) denote the nuclei of A and B, respectively, \(\mathbf{r}_{\alpha}\) and \(\mathbf{r}_{\beta}\)
denote the nuclear positions, \(v_{\text{ES}}(\mathbf{r})\) and \(v_{\text{ES}}(\mathbf{r})\) denote the electronic
densities, and \(v_{\text{ES}}(\mathbf{r})\) and \(v_{\text{ES}}(\mathbf{r})\) 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.\textsuperscript{5}

Often one can use the electrostatic potential alone, \textit{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

Differential
DIFFERENT USES OF THE ELECTROSTATIC POTENTIAL

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 \( V^{ES}(\rho) \) and the electron density function \( \rho(\mathbf{r}) \) contain equivalent information. The electrostatic potentials used for the applications discussed above6,7 were all obtained from quantum mechanical calculations of the electron density. It would be useful to be able to obtain accurate values of \( V^{ES}(\rho) \) or \( \rho(\mathbf{r}) \) directly from experiment to obviate these quantum mechanical calculations or to test their accuracy. As discussed next, information
about $\rho(\mathbf{r})$ 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 treat-
ment 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
separation 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 electro-
static 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 correlate 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 approximations 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. 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


DIFFERENT USES OF THE ELECTROSTATIC POTENTIAL


