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INTRODUCTION: THE ROLE OF THE ELECTROSTATIC
POTENTIAL IN CHEMISTRY

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The electrostatic potential at a point \vec{r} in the vicinity of an atomic or molecular system having an electronic density function $\rho(\vec{r})$ is given, in atomic units,* by

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

where Z_A is the charge on nucleus A, located at \vec{R}_A . The two terms on the right side of equation (1) correspond, respectively, to the nuclear and electronic contributions to the potential. As can be seen, they have opposite signs and accordingly opposite effects; $V^{ES}(\vec{r})$ represents the net result at any point \vec{r} . The electrostatic potential is a real physical property, which is rigorously defined by equation (1). It is exactly equal in magnitude to the electrostatic (coulombic) interaction energy between the static (*i.e.*, unperturbed) charge distribution of the system and a positive unit point charge located at \vec{r} .

*Atomic units are defined in the Preface, which also contains conversion factors to other systems of units.

In recent years, the electrostatic potential has emerged as a powerful tool for studying the properties of atoms and molecules on both fundamental and applied levels. Some of the factors that have brought about this new prominence are summarized briefly in this chapter; many of them are treated in more detail later in this book.

Since the electrostatic potential is very directly and rigorously related to the electronic density, both by equation (1) and also by Poisson's equation,

$$\nabla^2 V^{\text{ES}}(\vec{r}) = 4\pi\rho(\vec{r}) \quad (2)$$

it can be expected to play an important role in density functional theories. In view of equations (1) and (2), the density functional concept¹ that the energy of a system can be expressed as a functional of its charge density suggests investigating the possible existence of relationships between the energy of a system and its electrostatic potential. There have been some encouraging developments along these lines, on both exact and approximate levels. These are discussed in detail in the next two chapters, by Politzer and by Levy, Clement and Tal, and applications to atoms and molecules are presented. It is interesting that the energy can be related in particular to the electrostatic potentials at the nuclei in these systems. One form of such a relationship came already from the Thomas-Fermi method (an early example of a density functional theory), according to which the energy of a free atom with nuclear charge Z is given by²

$$E = \frac{3}{7} ZV_0^{\text{ES}} \quad (3)$$

in which V_0^{ES} is the electrostatic potential at the nucleus.

In addition to their fundamental importance, there are at least two very practical reasons for wanting to develop accurate and reliable expressions relating the total energy of a system to its electronic density or electrostatic potential. First, it is well known that some *ab initio* and semiempirical procedures for computing wave functions yield more accurate one-electron properties [such as $\rho(\vec{r})$ and $V^{\text{ES}}(\vec{r})$] than total energies. It has been shown, for example, that one-electron properties calculated with Hartree-Fock and other self-consistent-field wave functions that satisfy Brillouin's theorem are accurate to second order; *i.e.*, the first-order correlation correction vanishes.³ Semiempirical methods may also often yield more accurate one-electron properties than energies; *e.g.*, the extended-Hückel method can provide some useful one-electron properties, but it does not predict total energies directly.⁴ As a consequence, if the energy could be expressed sufficiently well

in terms of either the electronic density or the electrostatic potential, then in many cases better energies could be obtained indirectly, *via* $\rho(\vec{r})$ or $V^{ES}(\vec{r})$, than directly by the original wave function computation. Indeed, Levy, Clement and Tal have already succeeded in doing this for atomic systems, as they explain in Chapter 3.

Chapter 4, by Parr and Berk, is also closely related to the goals that we have just described. These authors show that one can calculate reasonably accurate electronic densities by taking as a starting point the electrostatic potential generated by only the nuclei of a molecule. The usual approach in computing molecular properties in quantum chemistry is to first compute an approximate wave function, and from it to obtain the electronic density and other properties, such as the electrostatic potential. Thus it is interesting to explore more fully the possibilities raised in these chapters of starting with an electrostatic potential and using it to determine other quantities, like total energies (as discussed in the previous paragraph) and electronic densities, as just mentioned. Still another example of this kind of relationship between properties is provided by the chapter of Bentley, which is concerned in a certain sense with calculating electrostatic potentials from electronic densities. In particular, he shows how to obtain a useful and reasonably accurate representation of $V^{ES}(\vec{r})$ from only the molecular geometry and the low-order molecular multipole moments of the electronic density.

A second practical reason for developing theories based on the electronic density and the electrostatic potential is that these quantities are real physical properties and can be determined experimentally by scattering techniques (X-ray or electron diffraction). The availability of reliable relationships between electrostatic potentials and total energies or interaction energies would therefore make it possible to go directly from the quantities obtained by these scattering experiments to the energetic quantities of interest to chemists.

X-ray diffraction directly explores the electronic density of the target material, because it is the electrons that scatter the X-ray photons. According to equation (1), this experimentally measured electronic density can be used to determine the electrostatic potential, the quantity with which we are primarily concerned here. This operation is discussed in Chapter 17 by Stewart and in Chapter 18 by Moss and Coppens.

In electron diffraction, it is the electrical potential of the target material that scatters the incident electrons. When these have high enough energies, in the 20-50 keV range, the electrical potential is well approximated by the electrostatic potential, as

expressed by equation (1); such complicating factors as exchange of target and incident electrons, and target charge polarization may be neglected. Experiments of this sort, which may be regarded as the direct experimental measurement of the electrostatic potential, are discussed in Chapter 7 by Fink and Bonham. Lower-energy electron scattering; in which both the electrostatic potential and also such other effects as exchange and polarization play important roles, is treated in Chapters 8 and 9. Chapter 6 considers in more detail the relationships between the roles of the electrostatic potential in the various kinds of scattering situations and in the treatment of molecular interaction energies.

It is important from a fundamental point of view that the electrostatic potential is directly measurable, but most applications so far have followed the conventional approach of calculating it from approximate wave functions. In principle, one should always increase the level of approximation and basis-set size until the calculated electrostatic potential has converged. In practice, this is of course often not feasible. Although Chapters 8 and 9 deal explicitly with electron scattering, they also treat two aspects of electrostatic potentials that are very important for other applications discussed in the book. Chapter 8 presents several examples showing how reasonably accurate molecular electrostatic potentials can be obtained from very simple approximations to the electronic density. Chapter 9 considers the importance of charge polarization in a molecule when it interacts with a charged species. In particular, large basis sets are used to calculate the polarization effect accurately, and it is shown that the role of polarization may be systematically underestimated if small basis sets are employed.

So far, this discussion has emphasized quantitative applications of the electrostatic potential, involving its relationships to other properties of chemical systems, such as energies, electronic densities and scattering amplitudes. However, very extensive use of electrostatic potentials has also been made on a more qualitative level, as guides to the reactive properties of molecules, especially toward electrophilic attack. By computing contour maps of the potentials in various planes through a molecule, one can see and compare the spatial regions in which the potential is negative and to which an electrophile would initially be attracted, and one can even obtain some idea of the most favored channels of approach to specific locations within these regions. Here the electrostatic potential is being used for somewhat the same purposes, although on a much more refined level, as are calculated atomic charges. In such applications, the potential has the advantage of being a real physical property, whereas atomic charges are necessarily arbitrarily defined; accordingly, the former leads, in general, to a more reliable and physically meaningful picture.

Since the electrostatic potential reflects the unperturbed charge distribution of just one of the partners in an interaction, it is expected to be most useful, as a guide to reactivity, in processes that do not involve large changes in the electronic density. Despite this limitation, the electrostatic potential has been found to be a very useful tool for understanding reactive properties and structures in a wide variety of situations.^{5,6} This type of application is covered in depth in the chapters by Tomasi, Morokuma, Kollman, Weinstein, Kaufman, the Pullmans, Kistenmacher, Liebman, and their collaborators. Among the topics that they treat are the chemistry of nucleic acids, molecular interactions with protons, metal ions, and metal-containing species, hydrogen-bonded complexes, other metal and donor-acceptor complexes, receptor selectivity and comparative biological properties of certain classes of drugs, reaction intermediates and transition states, carcinogens and their metabolites, intramolecular interactions, and molecular ionization potentials.

While the use of the electrostatic potential as a means of correlating and interpreting molecular reactivities is now well-established, it is essential to keep in mind the fact that the electrostatic potential of a chemical system is only one contributing factor in its interaction with some other entity. Even when the electronic density of the other reactant is quantitatively taken into account, so as to obtain the total electrostatic interaction energy between the two unperturbed charge distributions, there still remain such possibly important factors as polarization and/or charge transfer that have been neglected. It can therefore be extremely enlightening to carry out an accurate calculation and analysis of all of the contributions to the total interaction energy of two systems, including polarization, charge-transfer and exchange as well as electrostatic effects. In this way, one can often find better justification for interpretations based on the electrostatic potential alone, and at the same time learn more about its limitations. Such energy-component analyses have been developed extensively by Morokuma at the self-consistent-field level (*i.e.*, neglecting electron correlation), and they are discussed in the chapters by Morokuma and Kitaura, by Kollman, and by Tomasi.

In this introduction, we have tried to sketch the central concepts that provide a basic unity to this book. But the individual chapters, like the spokes of a wheel, head out in many directions and touch on many subjects that may be far removed from the unifying ideas at the center. We hope that putting these various contributions together in one volume will produce a stimulating overview of an exciting and rapidly developing field.

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