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Intermolecular Electrical Interaction: A Key Ingredient in Hydrogen Bonding

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Electrical interaction, meaning the interaction of fixed charge distributions as well as the polarization that may occur, is an established idea for understanding and interpreting certain molecular phenomena, with much of the foundation set in place by Buckingham.[1] It is most often invoked as some type of "electrostatic model", which is often as simple as the interaction of two permanent dipoles. Labeling any such treatment as a "model" usually means (1) that the interaction develops from a truncated expansion, or (2) that some of the electrical properties are assigned, estimated, or guessed, or (3) that adjustments are made to incorporate something that is outside classical electrostatics. Such models are commonplace; they are very much a tool for understanding experimental observations. Their use ranges from the orientations of molecules on surfaces,[2,3] hydrogen bonding,[4-10] lipid structure on liquid surfaces,[11] potentials for condensed-phase simulations,[12,13] molecular aggregation in low-density, interstellar clouds, and potentials for theoretical studies of molecular scattering.[14-16] The models give structural information, for the most part, and sometimes property information as well. They may lead to assignment of spectral features, perhaps by distinguishing whether the arrangement of two bonding species is more favorable linear or T-shaped. Electrical interaction ideas are frequently invoked, yet the extent of applicability and overall utility is still subject to investigation.

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Electrical or electrostatic interaction normally refers to a *classical* analysis of the interaction between two *separate* charge distributions, though the form of molecular charge distributions is dictated by quantum mechanical laws. At some point of approach of two species, a sharp change in individual electronic structures would call for incorporating intermolecular quantum features. Thus, penetration and the quantum feature of exchange repulsion cannot be neglected at short range or else a coalescence of species may be "predicted". At long range, electrical interaction persists even when quantum features have died off, and so at least there, it alone must prove satisfactory. The applicability of electrical analysis in intermediate regions is less certain, yet this is a very important region.

(1) Buckingham, A. D. *Adv. Chem. Phys.* **1967**, *12*, 107.
(2) Harris, A. B.; Berlinsky, A. J. *Can. J. Phys.* **1979**, *57*, 1852.
(3) You, H.; Fain, S. C., Jr. *Surf. Sci.* **1985**, *151*, 361.
(4) Kollman, P., *J. Am. Chem. Soc.* **1977**, *99*, 4875.
(5) Hurst, G. J. B.; Fowler, P. W.; Stone, A. J.; Buckingham, A. D. *Int. J. Quantum Chem.* **1980**, *29*, 1223.
(6) Buckingham, A. D.; Fowler, P. W. *Can. J. Chem.* **1985**, *63*, 2018.
(7) Rendell, A. P. L.; Bacskay, G. B.; Hush, N. S. *Chem. Phys. Lett.* **1985**, *117*, 400.
(8) Liu, S.-Y.; Dykstra, C. E. *Chem. Phys.* **1986**, *107*, 343.
(9) Buckingham, A. D.; Fowler, P. W.; Stone, A. J. *Int. Rev. Phys. Chem.* **1986**, *5*, 107.
(10) Cummins, P. L.; Rendell, A. P. L.; Swanton, D. J.; Bacskay, G. B.; Hush, N. S. *Int. Rev. Phys. Chem.* **1986**, *5*, 139.
(11) Keller, D. J.; McConnell, H. M.; Moy, V. T. *J. Phys. Chem.* **1986**, *90*, 2311.
(12) Thiery, M. M.; Chandrasekharan, V. *J. Chem. Phys.* **1980**, *73*, 3384.
(13) Stillinger, F. H.; David, C. W. *J. Chem. Phys.* **1980**, *73*, 3384.
(14) Truhlar, D. G.; Dixon, D. A.; Eades, R. A. *J. Phys. B* **1979**, *12*, 1913.
(15) Buck, U.; Schleusener, J.; Malik, D. J.; Secrest, D. *J. Chem. Phys.* **1981**, *74*, 1707.
(16) *Chemical Applications of Atomic and Molecular Electrostatic Potentials*; Politzer, P., Truhlar, D. G., Eds; Plenum: New York, 1981.

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The problem of weak attraction of two species, but not chemical bond formation, falls in this region. As a working definition, around 10 kcal/mol (or less) will define the well depth of "weakly" attractive species. This includes many cases of hydrogen bonding, where a proton of one molecule is the closest atom of that molecule to the weakly attached partner. It also includes other weak complexes, even those without intervening hydrogens. Indeed, one point of this report is that hydrogen bonding can be placed in a broader category of weak interaction, where electrical effects happen to be an essential ingredient.

In addition to evaluating interaction energies, electrical analysis naturally yields electrical properties of a complex. It is not clear if both types of predictions should be of equal reliability, and this is another way in which the applicability of electrical concepts has not been fully explored. Furthermore, even where electrical interaction does not dominate the energetics, its influence on properties might be dominant. Electrical analysis may well be capable of giving hard information on properties, a possibility that has been thought about for a long time.

Only now is the capability of quantitatively examining the ranges of applicability of electrical analysis and utilization of electrical models emerging. An obstacle had been a lack of sufficiently extensive sets of molecular electrical properties. New computational methods in ab initio electronic structure theory have overcome that obstacle. Within the self-consistent field (SCF) approximation at least, it is now possible to compute any desired multipole polarizability, hyperpolarizability, second hyperpolarizability, and so on. Another obstacle, evaluating electrical interaction with an extensive set of properties, has been overcome with special computational algorithms. This report is meant (1) to illustrate what electronic structure theory can do in finding electrical properties of molecules, (2) to indicate how electrical interaction can be computed, and (3) to show what electrical analysis tells in one specific area, hydrogen and weak bonding. It is tantalizing that simple electrical analyses might be used as reliably in many other circumstances and that either neglecting or else modeling intermolecular quantum features serves to extend the applicability.

Electrical Properties of Molecules

The understanding of molecular electrical interaction begins with the properties of isolated molecules. All electrical properties of a molecular charge distribution are formally defined as derivatives of the quantum mechanical molecular energy. Permanent moments are first derivatives. The differentiation is with respect to the elements of a power series expansion of an arbitrary external electrical potential, $V(x,y,z)$, such as the element $V_x \equiv \partial V/\partial x|_o$, where "o" is the origin of the expansion in the geometrical space. If one wished, some arbitrary potential could be constructed by specifying, relative to a chosen point in space, its uniform field components (e.g., V_x,V_y,V_z), its gradient components (e.g., V_{xx}, V_{xy}, V_{xz}, ...), and so on.

The energetic interaction of a fixed (unpolarizable) classical distribution of charges $\{q_i\}$ with a potential is simply $E^{int} = \sum_i q_i V(x_i,y_i,z_i)$, where (x_i,y_i,z_i) is the position of the q_i charge. In terms of the power series expansion, this is

$$E^{int} = V(o,o,o)\sum_i q_i + V_x\sum_i q_i x_i + V_y\sum_i q_i y_i + V_z\sum_i q_i z_i + \frac{1}{2}V_{xx}\sum_i q_i x_i^2 + \frac{1}{2}(V_{xy} + V_{yx})\sum_i q_i x_i y_i + \ldots + \frac{1}{6}V_{xxx}\sum_i q_i x_i^3 + \ldots \quad (1)$$

The summations in this equation are elements of the moments of the charge distribution, referred to as multipoles. The multipoles can be defined with a number of conventions,[1,17,18] but one advocated by Applequist[18,19] collects up everything in a given term of eq 1 that is not a V parameter. For instance, $M_{xxx} \equiv {}^1/_6 \sum_i q_i x_i^3$. Equation 1 then takes on a particularly simple form.

$$E^{int} = V(o,o,o)M_o + V_xM_x + V_yM_y + V_zM_z + V_{xx}M_{xx} + \ldots \quad (2)$$

Clearly, in this expression each multipole element, M_α, is a first derivative of the energy with respect to the associated parameter, V_α. Also, eq 2 is a simple dot product of a "vector" $\mathbf{V} = (V_o,V_x,V_y, \ldots)$ and a "vector" $\mathbf{M} = (M_o,M_x,M_y, \ldots)$, which is nice for computing.

The second derivatives of E^{int} are zero because it was assumed that the point charges, q_i, were fixed in space (i.e., a nonpolarizable charge distribution). Were it polarizable, as a real molecule certainly is, a general picture of the response to an external potential can be given in the form of all second and higher derivatives of the energy with respect to the parameters in $\mathbf{V}$. For any such parameter, there is an associated multipole tensor element. For instance, $\partial^2E^{int}/(\partial V_x\,\partial V_{xx})$ is a dipole–quadrupole (first and second moment) polarizability tensor element. $\partial^2E^{int}/(\partial V_x\partial V_y)$ is an element of the dipole polarizability tensor, usually designated α.

Molecular spectroscopy, primarily via Stark effect, electric deflection, and light scattering, has given most of the current knowledge of electrical properties of atoms and small molecules. Unfortunately, these laboratory measurements rarely give more than the first and second moments and the dipole polarizability, and that is rather incomplete for assessing electrical interaction. Here, theoretical chemistry and computational chemistry are providing important data by finding higher moments, other multipole polarizabilities, and hyperpolarizabilities. The laboratory data, of course, provide the essential benchmarks for devising and checking the theoretical means of evaluation.

The advance in ab initio quantum chemistry making it possible to obtain electrical properties is the development of derivative techniques.[20–22] The properties of interest are derivatives of the energy, and so derivative Schrodinger equations must be solved. These are generated by differentiation with respect to the parameters in $\mathbf{V}$ when the Hamiltonian includes the interaction operator $\mathbf{V}\cdot\hat{\mathbf{M}}$ and $\hat{\mathbf{M}}$ contains the quantum

(17) McLean, A. D.; Yoshimine, M. *J. Chem. Phys.* **1967**, *46*, 3682.
(18) Applequist, J. *Chem. Phys.* **1984**, *85*, 279.
(19) Applequist, J., *J. Math. Phys.* **1983**, *24*, 736; *J. Chem. Phys.* **1985**, *83*, 809.
(20) *Geometrical Derivatives of Energy Surfaces and Molecular Properties*; Jorgensen, P., Simons, J., Eds.; Reidel: Dordrecht, 1986.
(21) King, H. F.; Komornicki, A. *J. Chem. Phys.* **1986**, *84*, 5645.
(22) Handy, N. C.; Schaefer, H. F., III. *J. Chem. Phys.* **1984**, *81*, 5031.

mechanical multipole moment operators. Differentiation of the $H\Psi = E\Psi$ with respect to a and b, arbitrary elements of **V**, yields

$$H^a\Psi + H\Psi^a = E^a\Psi + E\Psi^a \quad (3a)$$

$$H^{ab}\Psi + H^a\Psi^b + H^b\Psi^a + H\Psi^{ab} = E^{ab}\Psi + E^a\Psi^b + E^b\Psi^a + E\Psi^{ab} \quad (3b)$$

Solving eq 3a yields E^a, a permanent moment, and Ψ^a. From eq 3b, one obtains E^{ab}, a polarizability. Entirely analogous to perturbation theory, finding a derivative wave function of some order n is the primary step for finding energy derivatives of order $2n + 1$. First derivatives of the energy, the permanent moments, are equal to the expectation value of the moment operator if the Hellmann–Feynman theorem is satisfied; it is for SCF and full-Cl wave functions. For other well-correlated wave functions expectation values should be very close to the derivative valuation.

Electron correlation, the computationally laborious step in electronic structure calculations, plays a role in molecular electrical properties. In evaluating electrical interaction, the typical ~5%[23] correlation effect on permanent moments is more important than the ~10% effect on polarizabilities[24-27] because the moments are more important in the interaction energies. At the SCF level, derivative techniques have been developed to a very high level of sophistication. The derivative Hartree–Fock (DHF) approach[28] has been implemented to solve a derivative Hartree–Fock equation of *any* order, with any number of multipoles or **V** parameters. It is a truly open-ended procedure and many calculations have been carried out already.[23]

Very extended basis sets are required for calculations of polarizabilities and hyperpolarizabilities. DHF is open-ended with respect to basis set size as well, and calculations on benzene have been carried out with a sizable basis of ~200 functions. This capability means that in terms of basis set limitations, the electrical properties that go into the classical interaction evaluation can be obtained better than quantum mechanical evaluation of the interaction. For a hydrogen-bonded dimer such as $(HF)_2$, the ab initio quantum mechanical energy requires a basis set twice that for finding the electrical properties of one HF, or twice that required for electrical analysis of corresponding basis quality. We have used very large basis sets to find electrical properties of isolated monomers, but correspondingly large bases have not yet been used to find ab initio potential surfaces of dimers. In many ab initio studies, the bases that are being employed may prove too small to fully account for electrical interaction.

Electronic structure calculations are based in the Born–Oppenheimer approximation, which means that molecular energies, permanent moments, polarizabilities, and so on are determined for specific geometrical structures. Equilibrium properties are the ones most commonly reported. For one-dimensional vibrational problems, the derivative Numerov–Cooley (DNC) method[29] is a calculational process for rigorously evaluating pure vibrational effects on electrical properties. DNC solves the derivative Schrodinger equations for the vibrational wave functions, and like DHF, it is open-ended. In this way, electrical properties have been obtained for manifolds of vibrational states of diatomic molecules, and so electrical analysis can be carried out monomers in particular vibrational states. Table I lists values of electrical properties for two diatomics as examples of calculations.

Table I
Examples of Calculated Electrical Properties[a]

molecule	property	theor value[c]	expt[c]
HF	μ_eD	1.807 [30]	1.803 [31]
	$eqQ_{(v=0)}$,[b] kHz	351.0 [32]	354.238 [33]
	γ_{zzzz}, au	262.9 [34]	
N_2	θ, au	−1.085 [34]	−1.09 [35]
	$\alpha_\parallel$, au	14.83 [34]	
	$\alpha_\perp$, au	9.66 [34]	
	$\bar{\alpha}$, au	11.38 [34]	11.74 [36]

[a] The polarizabilities were calculated with the ELP extended basis sets[34] with DHF. The other properties were obtained with basis sets of at leat the quality of a doubly-polarized, triple-ζ (TZ2P) set and included electron correlation effects at the ACCD (coupled cluster) level. [b] For deuterium in DF. [c] Literature references are given in brackets.

Classical Electrical Interaction between Polarizable Charge Distributions

Outside a molecular charge distribution, the potential $V(x,y,z)$ is equivalent to that arising from point multipoles whose sizes are that molecule's multipole moments evaluated at the geometrical point corresponding to the multipole moment expansion center. If $\mathbf{r} = (x,y,z)$ is an arbitrary vector from that center, the potential at **r** is

$$V(x,y,z) = \mathbf{T}\cdot\mathbf{M} \quad (4)$$

where **T** is the array of values defined by the following sequence.

$$T_0 = |\mathbf{r}|^{-1} \quad (5)$$

$$T_x = -\frac{\partial}{\partial x}|\mathbf{r}|^{-1}$$

...

$$T_{xx} = \frac{\partial^2}{\partial x^2}|\mathbf{r}|^{-1}$$

$$T_{xy} = \frac{\partial^2}{\partial x \partial y}|\mathbf{r}|^{-1}$$

...

$$T_{xxx} = -\frac{\partial^3}{\partial x^3}|\mathbf{r}|^{-1} \quad \text{and so on}$$

(23) Dykstra, C. E.; Liu, S.-Y.; Malik, D. J. *Adv. Chem. Phys.*, in press.
(24) Werner, H.-J.; Meyer, W. *Mol. Phys.* **1976**, *31*, 855.
(25) Bartlett, R. J.; Purvis, G. D. *Phys. Rev.* **1979**, *A20*, 1313.
(26) Amos, R. D. *Chem. Phys. Lett.* **1980**, *70*, 613; **1982**, *88*, 89.
(27) Maroulis, G.; Thakkar, A. *J. Chem. Phys.* **1988**, *89*, 7623.
(28) Dykstra, C. E.; Jasien, P. G. *Chem. Phys. Lett.* **1984**, *109*, 388.
(29) Dykstra, C. E.; Malik, D. J. *J. Chem. Phys.* **1987**, *87*, 2806.
(30) Bernholdt, D. E.; Liu, S.-Y.; Dykstra, C. E. *J. Chem. Phys.* **1986**, *85*, 5120.
(31) Gough, T. E.; Miller, R. E.; Scoles, G. *Faraday Discuss. Chem. Soc.* **1981**, *71*, 77.
(32) Liu, S.-Y.; Dykstra, C. E. *Chem. Phys.* **1987**, *115*, 461.
(33) Muenter, J. S.; Klemperer, W. *J. Chem. Phys.* **1970**, *52*, 6033.
(34) Liu, S.-Y.; Dykstra, C. E. *J. Phys. Chem.* **1987**, *91*, 1749.
(35) Buckingham, A. D.; Graham, C.; Williams, J. D. *Mol. Phys.* **1983**, *49*, 703.
(36) Alms, G. R.; Burnham, A. K.; Flygare, W. H. *J. Chem. Phys.* **1975**, *63*, 3321.

With a multipole expansion, the potential due to A at the multipole center of B is found, as well as the potential due to B at A. The permanent moment interaction between A and B is found by using an expression such as eq 2. It must be realized that through the elements of **T**, a moment of one type on A may interact with a moment of another type on B.

The multipole expansion can be continued to very high order in new computational procedures,[37] but it still is a truncated expansion subject to two formal limitations. First, quantum mechanical charge distributions extend, at least with small density, well away from a molecule's nuclear skeleton, and so it is only approximately true that the charge distributions of two weakly bound molecules are not overlapping or not penetrating. Second, there is no assurance that the separation distance between molecules A and B is large enough for the multipole expansion to be convergent. Some tests[38] do show a declining energy contribution from higher moments in small-molecule dimers, but this is partly related to molecular size. With greater size comes the prospect for much larger, higher moments. Physically, this amounts to saying that it would be difficult to represent the potential of an extended, ~ 100-atom molecule by just several ideal point multipoles at the center of the molecule. Even a molecule as small as benzene has a hexadecapole (fourth) moment that is sizable in intermolecular interactions. An excellent solution to this limitation is to represent a large molecule by lower order multipoles at many centers distributed through molecule. Stone has formulated ways of accomplishing this and has carried out quite a number of calculations of this sort.[39,40] So, while there are formal concerns about the limitations of multipole expansions, the practical situation appears clearer and more optimistic.

Polarization of charge, which comes about as the molecule experiences a potential, means that the potential it creates is no longer that due to the permanent moments. There arises, then, a set of coupled equations for mutual polarization of two (or more) molecules. These are easily solved by iterative treatments,[37] which yield not only the energy of polarization but also the induced multipoles and induced polarizabilities of each molecule. An induced dipole polarizability of A is the product of the uniform field at A due to molecule B with the dipole *hyper*polarizability of A.

An interesting test calculation[41] we carried out a few years ago lends much encouragement to the use of electrical interaction to generate weak bonding potentials. In this calculation on $(HF)_2$, a classical analysis was carried out to find the induced dipoles, induced polarizabilities, and even the induced hyperpolarizability. The total dipole hyperpolarizability tensor of the complex was mapped out as a function of the intermolecular separation distance. As shown in Figure 1, at least one element of the dipole hyperpolarizability tensor was sensitive to hydrogen bond formation, and the classical determination of that sensitivity was very much in agreement with what was found with a full quantum mechanical evaluation. It is unlikely that there could be this agreement unless it is true that the primary change in a molecule's electronic structure upon weak bonding is just polarization of charge. And if that is true, then there must be tools for reliably studying the interactions that are much simpler than full quantum mechanical treatments.

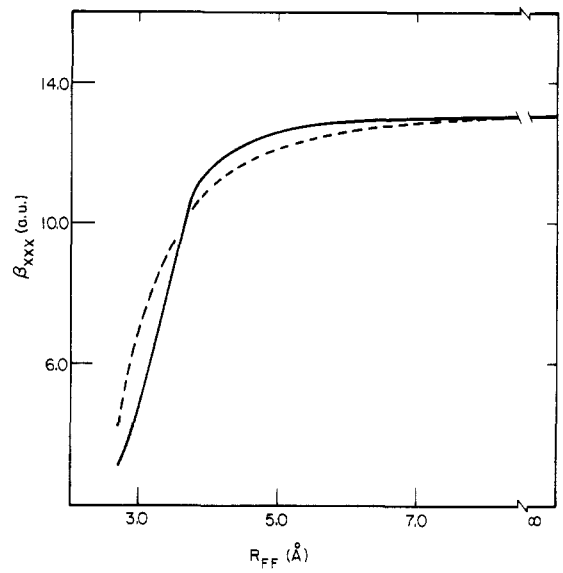

Figure 1. Axial dipole hyperpolarizability element, β_{xxx}, of the HF dimer as a function of the fluorine separation distance.[41] The x axis is defined by the line connecting the fluorine centers. The solid line is the ab initio result, while the broken line is obtained from a classical analysis of the intermolecular interaction.

Nonelectrical Contributions to the Potential

The partitioning of the water–water hydrogen bond energy that Coulson outlined decades ago[42] has been the template for many theoretical analyses of contributing effects. Coulson identified electrical interaction and also exchange repulsion and dispersion, which are pure quantum features. An important conclusion that Coulson reached without the benefit of high-powered computation is that the contributing terms to the hydrogen bond energy may be of similar size, with some being attractive and some repulsive. This still seems true, but now can be made more quantitative.

It is often found that electrical interaction energies at an equilibrium structure of a weak complex are very similar to ab initio values of the stability. Furthermore, the changes in the potential for small reorientations of a molecule in a complex, at some fixed separation distance, are usually rather nicely described by electrical interaction, using high-level ab initio calculations to check. Thus, no matter what the size of other possible effects, a certain balance must exist that allows for their collective neglect for certain potential surface features. However, this does not say that the stabilization should be regarded as solely electrical. Also, for certain features, such as the radial dependence of the interaction potential, this neglect proves totally unwarranted.

Global potential surfaces for hydrogen-bonded complexes are essential to extract the most understanding out of the intricate spectroscopic experiments that have opened up this field. The challenge, then, is to see if nature has provided an easy way to find these surfaces,

(37) Dykstra, C. E. *J. Comput. Chem.* **1988**, *9*, 476.
(38) Dykstra, C. E. *J. Phys. Chem.* **1987**, *91*, 6216.
(39) Stone, A. *J. Chem. Phys. Lett.* **1983**, *83*, 233.
(40) Stone, A. J.; Alderton, M. *Mol. Phys.* **1985**, *56*, 1047.
(41) Dykstra, C. E.; Liu, S.-Y.; Malik, D. J. *J. Mol. Struct. (Theochem)* **1986**, *135*, 357.
(42) Coulson, C. A. *Research* **1957**, *10*, 149.

Table II
Comparison of Vibrational Parameters of Ar-Ar Potentials

		potential				
	R_{eq}, Å	$\langle R^{-2}\rangle_{v=0}^{-1/2}$, Å	$\langle R^{-2}\rangle_{v=1}^{-1/2}$, Å	$E_{v=0}$, cm^{-1}	$E_{v=1}$, cm^{-1}	$E_{v=2}$, cm^{-1}
eq 6[a]	3.7294	3.8012	3.9706	15.94	42.76	63.38
ref 43[a]	3.7550	3.8210	3.9756	14.85	40.52	60.99

[a] Numerov–Cooley vibrational analysis[44] was carried out for equivalent functional fits with like data points for each potential.

or if laborious ab initio calculation is the only hope. Electrical analysis is easy in terms of computation. It includes nonpairwise interactions and so it can display cooperativity effects that would be lacking in force field potentials. Augmentation of electrical potentials might make them suitable even where other contributors to the interaction do not remain in balance, such as along a radial coordinate on the potential energy surface. Buckingham and Fowler have done this by using infinitely hard wall potentials that keep apart molecules in weakly bonded complexes; permanent moments give the electrical and attractive potential.[6]

The electrical interaction studies central to this discussion involve permanent moment interactions plus the more subtle effects of polarization. At this level of detail, it is appropriate to go beyond an infinitely hard, repulsive potential in augmenting electrical interaction to make global potential surfaces calculable. A soft-edge wall potential that has been used in several calculations is the following.

$$V' = \sum_{i}^{\{A\}}\sum_{j}^{\{B\}}\left[c_i c_j(e^{-\xi_i(r_{ij}-R_i-R_j)} + e^{-\xi_j(r_{ij}-R_i-R_j)}) - \frac{d_i d_j}{r_{ij}^6}\right] \quad (6)$$

The sums are over the atoms in molecules A and B; r_{ij} is the distance between the i atom in A and the j atom in B. R_i are atomic radii. Notice that for a rare gas interaction potential, there is no classical electrical contribution. Thus, the empirical potential of eq 6 must provide the full description of an Ar–Ar or Ne–Ne potential in this model. This fact has offered a starting point for the selection of the parameters in the augmenting potential. For Ar_2 parameters in eq 6 were adjusted to give the best agreement with the potential from spectroscopic analysis.[43] Table II summarizes the comparison and shows how nicely this standard type of empirical potential performs. Next, mixed complexes such as Ar–HF and Ar–HCN have been used to determine the best parameters for atoms of other species (e.g., HF and HCN), relying on available experimental data and high-level ab initio results. Unlike Ar_2, it is the sum of the empirical and electrical potentials that is tested, and so the parameters may show some dependence on the truncation levels of the chosen electrical treatment. The augmenting potentials are of use only if they are transferable, and so tests and adjustments are made in comparison with several complexes, such as HF in Ar–HF, in $(HF)_2$, and in N_2–HF. Examples of values used are for Ar, $c = 0.132$, $d = 9.36$, $\xi = -2.39$ au, $R = 1.83$ Å, and for F, $c = 0.0113$, $d = 1.85$, $\xi = -2.39$ au, $R = 1.68$ Å. Empirically augmenting electrical potentials may also correct intrinsic deficiencies in the electrical analysis. If simple, transferable potentials manage to overcome errors in the electrical part of the potential while also accounting for everything nonelectrical, then the challenge to find simple means of generating global interaction potentials will have been met.

Studies of Weakly Bonded Clusters

Perhaps 100 binary complexes have been examined by electrical analysis (for example, ref 6–10, 37–41, and 45–47) and about 40 with the specific approaches discussed here. There is now very convincing information that suitably complete electrical analysis can account for orientational aspects of the structures of complexes. Some cases are very obvious: NN–HF is a linear structure, with the strongest interaction being between the dipole of HF and the quadrupole of N_2. HCCH–HF, though isoelectronic, is T-shaped since the sign of the quadrupole of HCCH is opposite that of N_2. Less simple is $(HF)_2$ whose bent structure is semiquantitatively predicted (to ~10°) by the juxtaposition of dipole–dipole forces favoring a linear structure, dipole–quadrupole forces favoring a 90° structure, and quadrupole–quadrupole forces that favor a T-shaped structure.[41] Polarization effects alter the equilibrium angles by no more than a few degrees.[38]

One puzzling complex is the ammonia dimer, where the disagreement between one electrical picture[49] and experimental structure determinations[50] is ~30°, a sharp qualitative difference to some. The electrical analysis, carried out for orientational slices through the potential energy surface at a fixed mass-center separation distance, was truncated at the third permanent moment with dipole and quadrupole polarizabilities and the dipole hyperpolarizability included. A wall potential was not used, though the steric consequences of the monomer shapes might be an element in the optimum structure. At issue is how the internal C_3 symmetry axes of the two ammonias point relative to the line connecting their mass centers. Pure electrical analysis shows a strong coupling of these two angles as well as coupling with the twist angles about each C_3 axis. The spectroscopically determined, on-average angles present the ammonias' C_3 axes (or the nitrogen lone pairs) as pointing by almost equal amounts above the line of the mass centers, for one, and below, for the other. Electrically, the ammonias are not so nearly equivalent, one C_3 axis rotated clockwise by about 30° and the other counterclockwise relative to the experimental structure. Ab initio[51–53] and electrical studies[49] both reveal con-

(43) Colbourn, E. A.; Douglas, A. E. *J. Chem. Phys.* **1976**, *65*, 1741.
(44) Cooley, J. W. *Math. Comput.* **1961**, *15*, 363.
(45) Buckingham, A. D.; Fowler, P. W. *J. Chem. Phys.* **1983**, *79*, 6426.
(46) Dykstra, C. E. *Chem. Phys. Lett.* **1987**, *141*, 159.
(47) Legon, A. C.; Millen, D. J. *Proc. R. Soc. London, A* **1986**, *404*, 89.
(48) Dyke, T. R.; Howard, B. J.; Klemperer, W. *J. Chem. Phys.* **1972**, *56*, 2442.
(49) Liu, S.-Y.; Dykstra, C. E.; Kolenbrander, K.; Lisy, J. M. *J. Chem. Phys.* **1986**, *85*, 2077.
(50) Nelson, D. D., Jr.; Fraser, G. T.; Klemperer, W. *J. Chem. Phys.* **1985**, *83*, 6201; *Science (Washington, D.C.)* **1987**, *238*, 1670.
(51) Latajka, Z., Scheiner, S. *J. Chem. Phys.* **1986**, *84*, 341.
(52) Frisch, M. J.; Del Bene, J.; Binkley, J. S.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *84*, 2279.
(53) Sagarik, K. P.; Ahlrichs, R.; Brode, S. *Mol. Phys.* **1986**, *57*, 1297.

Table III
Stabilities of Weakly Bound Complexes

complex	stabilities (in cm^{-1}) electrical[a]	ab initio[a]	exptl[a]
H_2–HF	342 [30]	306 [30]	
N_2–HF	572	795 [54]	618 [55]
HF–HF	1700	1600 [56]	
HCN–HF	2490	2307 [54]	2180 [57]
$(HF)_3$	5460 [39]	4900 [56]	

[a] Literature references are given in brackets.

siderable flatness in this surface, and on a flat surface small correction potentials, perhaps a wall potential, can shift equilibrium geometries sharply. It is not known if the problem with $(NH_3)_2$ is a blatant failure of the electrical picture—we doubt that—or whether the unaugmented electrical treatment is finding only the gross features, i.e., flatness of the surface. Also, the flat potential implies wide-amplitude vibrational motion, and so completely resolving the disagreement with laboratory results may call for intricate dynamical analysis.

As already mentioned, electrical interaction energies at equilibrium structures are often similar to known stabilities of small clusters, and a few examples are in Table III. While this reinforces the importance of electrical effects, stabilities alone are an insufficient basis for assessing roles of contributing effects. Coulson's early analysis[42] made that apparent. A better basis is how the potential surface is shaped, i.e., whether an electrically based model will generate a surface that is faithful in shape and form to the true potential energy surface. Were it not for the computing demands of the top-level ab initio treatments, they would provide the surfaces to compare with. The best hope right now is using experimental data and deducing potential surface information.

In a recent study of the cyclic trimer $(HF)_3$,[58] a detailed vibrational analysis truly tested the shape of an electrical potential surface, and the results compared beautifully with vibrational spectroscopic work done in concert.[58] Surfaces were generated for a fixed monomer mass-center separation distance, and no empirical wall potential was included. The first three moments and polarizabilities through the dipole hyperpolarizability were used to represent each HF electrically. Two enormous surfaces of over 10 000 grid points each were generated (in just hours of VAX 11/780 time!) for grids over three in-plane orientational angles or over three out-of-plane angles. A vibrational Hamiltonian matrix was constructed for a very large basis of product rotor functions and diagonalized to yield a manifold of torsional state energies.

Table IV lists results of calculations with two electrical surfaces, the first obtained with only the permanent moments, and the second with incorporation of polarization. The with-polarization treatment agreed very well with the gas-phase overtone IR transition frequencies that were measured.[58] (Actually, the assignment of the two overtones was made by using the theoretical treatment to predict the corresponding frequencies for isotopically substituted $(HF)_3$ and finding those in the laboratory.) The permanent moment surface yields frequencies that are too low, while ab initio harmonic frequencies are not suitable for understanding the measured spectra. So, polarization must affect the shape of the orientational part of the interaction potential in an important way. This fits the idea that the primary change in a molecule's electronic structure upon weak bonding is charge polarization.

As interaction gets stronger, the prospect increases for electronic structure changes more drastic than polarization. Charged–neutral species, with stronger than neutral–neutral interaction, are a testing ground. Our calculations[61] on one system, H_3^+ with H_2, are exciting in that the electrical potential closely follows the ab initio potential inward until almost the minimum is reached, a behavior typical of neutral–neutral potentials. Polarization may again be the primary electronic structure change.

An interesting manifestation of hydrogen bonding we have considered through electrical analysis is the shift in transition frequencies of intramolecular vibrations.[62] Electrical influence of molecule A on B changes during the course of B's vibration(s) because the permanent moments and polarizabilities of B are dependent on the geometrical parameters of B. So, A's electrical influence will change B's vibrational potential. If the primary electronic structure change upon weak bond formation is charge polarization, it is natural to expect such electrical influence would be a primary influence on the intramolecular potentials. Our first model[62] of this used a linear perturbative correction to a diatomic's stretching potential generated from electrical analysis. The simplicity of the scheme means there are limitations, as itemized recently,[63] yet it gave meaningful results for a series of binary HF complexes. The typical error in a computed transition frequency shift was 20%.

A more sophisticated approach, our second model, of the electrical influence on intramolecular vibration uses electrical properties for specific vibrational states of a constituent species. For diatomics, these are computed with DNC theory.[29] For example, the electrical interaction of (equilibrium) CO_2 with HF in its ground vibrational state ($v = 0$) is found to be 43 cm^{-1} different than with HF in the first excited vibrational state ($v = 1$). This difference is the predicted red shift in the $v = 0 \rightarrow 1$ HF stretching transition upon complexation with CO_2. The gas-phase value obtained by Nesbitt and co-workers is 57 cm^{-1}.[64] Electrical calculations also give a dipole moment value of the complex in good agreement with experiment: 2.206 vs 2.247 D.[65]

A fundamental issue in weak interaction is cooperativity. Polarization is at least quadratic in the field, and

(54) Benzel, M. A.; Dykstra, C. E. *J. Chem. Phys.* **1983**, *78*, 4052; **1984**, *80*, 3510E.
(55) Soper, P. D.; Legon, A. C.; Read, W. G.; Flygare, W. H. *J. Chem. Phys.* **1982**, *76*, 292.
(56) Liu, S.-Y.; Michael, D. W.; Dykstra, C. E.; Lisy, J. M. *J. Chem. Phys.* **1986**, *84*, 5032.
(57) Legon, A. C.; Millen, D. J.; Rogers, S. C. *Proc. R. Soc. London, A* **1980**, *370*, 213.
(58) Kolenbrander, K.; Dykstra, C. E.; Lisy, J. M. *J. Chem. Phys.* **1988**, *88*, 5995.
(59) Gaw, J. F.; Yamaguchi, Y.; Vincent, M. A.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1984**, *106*, 3133.
(60) Andrews, L.; Bondybey, V. E.; English, J. H. *J. Chem. Phys.* **1984**, *81*, 3452.
(61) Augspurger, J. D.; Dykstra, C. E., to be published.
(62) Liu, S.-Y., Dykstra, C. E. *J. Phys. Chem.* **1986**, *90*, 3097.
(63) Anex, D. S.; Davidson, E. R.; Douketis, C.; Ewing, G. E. *J. Phys. Chem.* **1988**, *92*, 2913.
(64) Lovejoy, C. M.; Schuder, M. D.; Nesbitt, D. J. *J. Chem. Phys.* **1986**, *86*, 5337.
(65) Baiocchi, F. A.; Dixon, T. A.; Joyner, C. H.; Klemperer, W. *J. Chem. Phys.* **1981**, *74*, 6544.

Table IV
Torsional Vibrational Frequencies[a] (cm^{-1}) of $(HF)_3$

	theor freq			exptl freq	
	ab initio[b]	permanent moments	polarized surface	Ne matrix[c]	IR–IR double resonance
		In Plane			
$A'(\nu_{A'}=1,\nu_{E'}=0)$	897	703	801		
$E'(\nu_{A'}=0,\nu_{e'}=1)$	535	429	491	477	
$E'(\nu_{A'}=0,\nu_{E'}=2)$		826	955		941
		Out of Plane			
$A''(\nu_{A''}=1,\nu_{E''}=0)$	664		568	590	
$E''(\nu_{A''}=0,\nu_{E''}=1)$	449		376		
$E''(\nu_{A''}=1,\nu_{E''}=1)$			923		955

[a] From ref 58 except where indicated. [b] DZP/SCF values of *harmonic* frequencies (ref 59). [c] From ref 60.

for complexes, the field is a sum arising from all proximate molecules. Consequently, the field of molecule C may augment or diminish the polarizing effect of B on A (by adding to B's field) in an ABC complex. Electrical calculations have shown that this cooperativity extends the electrical influence of a polar species noticeably.[38] That cooperativity in weak interactions should be largely associated with polarization and not some other process is consistent with the earlier statement that the electronic structure change upon weak complexation is polarization. The success of a polarized electrical model in the torsional potentials of $(HF)_3$ encourages one to believe this, but much testing is called for. The recent microwave spectroscopic work of Gutowksy and co-workers[67] on the structures of trimer, tetramer, and pentamer complexes is providing certain information to test against. Corresponding electrical calculations are under way and, using the new computational scheme,[37] have extended to clusters with 87 constituent species so far.

Concluding Remarks

Hydrogen bonding is really part of a broader category of weak bonding, where electrical interaction dictates monomer electronic structure changes to a good extent. Through theoretical efforts on several fronts, a technology is taking shape to use this conclusion in a practical way, for the fast calculation of realistic potential surfaces and properties. But the successes to date may be eclipsed as optimum levels of truncating the expansions are established, or as the best transferable potentials for nonelectrical effects are worked out. We do not yet know how far the utility of electrical models will extend. Does it apply to stronger interactions such as those involving charged species or surfaces? Will it lead to correct predictions of intermolecular vibrations? What it could provide is a uniform basis for understanding weak molecular interaction from the limit of a pair of gas-phase molecules to condensed phases.

The explosion of spectroscopic work on hydrogen-bonded complexes at Illinois brought on by the late W. H. Flygare's development of pulsed beam, Fourier transform microwave spectroscopy was strongly felt in the theory complex in Noyes Lab. My group's work in this area began then. In the years since, discussions with a number of experimentalist colleagues have been truly stimulating and helpful, especially with Professor R. B. Bernstein, Dr. L. W. Buxton, Professor H. S. Gutowsky, Dr. K. Kolenbrander, Professor J. M. Lisy, and Dr. W. G. Read. Collaborative studies with Professor D. J. Malik have been extremely useful for the overall picture presented here. Several students in my group, Dr. M. A. Benzel, D. E. Bernholdt, Dr. P. G. Jasien, and Dr. S.-Y. Liu, are warmly thanked for their efforts on projects connected with or at the focus of this area. Support from the Chemical Physics Program of the National Science Foundation has been crucial for the developments reported here. Also, the donors of the Petroleum Research Fund, administered by the American Chemical Society, are gratefully acknowledged for grants that supported, in part, some of this work.

(66) Altman, R. S.; Marshall, M. D.; Klemperer, W. *J. Chem. Phys.* **1982**, *77*, 4344.

(67) Gutowsky, H. S.; Klots, T. D.; Chuang, C.; Schmuttenmaer, C. A.; Emilsson, T. *J. Chem. Phys.* **1985**, *83*, 4817; **1987**, *86*, 569. Gutowksy, H. S.; Klots, T. D.; Chuang, C.; Keen, J. D.; Schmuttenmaer, C. A.; Emilsson, T. *J. Am. Chem. Soc.* **1985**, *107*, 7174; *J. Chem. Phys.* **1987**, *87*, 4383. Gutowsky, H. S.; Chuang, C.; Klots, T. D.; Emilsson, T.; Ruoff, R. S.; Krause, K. R. *J. Chem. Phys.*, in press.