POTENTIAL ENERGY AND FORCE CONSTANTS OF A POTASSIUM CHLORIDE MOLECULE
FROM EXTENDED HÜCKEL CALCULATIONS

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Potential Energy and Force Constants of a Potassium Chloride Molecule
From Extended Hückel Calculations*

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Abstract

The potential energy and vibrational force constants of a potassium chloride molecule are calculated by the extended Hückel molecular orbital method using analytic approximations to the Hartree-Fock atomic orbitals in the computation of overlaps. The addition of a simple Coulomb attractive energy to the repulsive extended Hückel energy yields total potential energies in reasonable agreement with the experimental energy curve.

I. Introduction

This paper extends previous work examining the adequacy of extended Hückel calculations of atomic interaction energies for noble gas molecules¹ to the case of small ionic molecules. Extended Hückel theory² is a simple semi-empirical molecular orbital method which is capable of giving good approximations to the electronic structure of large molecules. Although it yields reasonable values for the potential energies associated with angular displacements, it does not give sufficiently good potential energies for bond stretching displacements to allow calculation of reasonable force constants. In a previous paper we discussed some modifications of the standard extended Hückel methods which improve the calculated values for repulsive potential energies associated with distance in pairs of noble gas atoms. The present paper extends the calculations to the potassium chloride molecule, with additional modifications to include ionic attraction. We feel this calculation illustrates most of the problems which would be encountered in extended Hückel calculations on ionic solids.

It is anticipated that there are two major contributions to the interaction energy of KCl: the attraction between the positive K ion and the negative Cl ion, and the repulsion due to the overlap of the electron distributions of the ions' closed shells. Both of these effects are frequently omitted in standard applications of extended Hückel theory. In its completely ionized state K^+Cl^- consists of two singly charged ions, each with the closed shell electron configuration of argon. For this configuration we calculate the closed shell's contribution to the energy as in reference 1, by extended Hückel calculations with basis sets consisting of analytic approximations to the Hartree-Fock atomic orbitals. The contributions of the ionic charges to both the total energy and to the atomic orbital energy parameters are represented

by simple Coulomb terms.

The possibility of incomplete ionization and the resulting covalent interaction is allowed for by inclusion of the potassium 4s state in the extended Hückel calculation. The calculated occupation of this state proves to be so small that the higher excited states of potassium are neglected. Two body electrostatic interaction energies as discussed by Anderson and Hoffmann³ appear to be small for this case and are also neglected.

The next section discusses the method used to apply extended Hückel theory to this small ionic molecule. Results, including potential energies and force constants, are presented in Section III. Justifications for some of the initial assumptions in the method are discussed in light of the results in Section IV.

II. Method

Extended Hückel molecular orbitals and energies are calculated for several KCl atomic separations ranging to .6 Å on either side of the equilibrium separation. The basis set consists of the valence shell 3s and 3p orbitals for chlorine, and the inner shell 3s and 3p orbitals and the 4s valence orbital for potassium. The diagonal energy parameters are orbital eigenvalues from atomic self-consistent field calculations by Bagus⁴ for K^+ and Cl^- , to which we have added a Madelung correction. The importance of including Madelung corrections to orbital energies for charged atoms has been emphasized by Corrington and Cusachs⁵, who point out that the neglect of Madelung corrections in charge dependent calculations leads to unrealistic final charge states. The Madelung correction shifts the orbital energies to account for the presence of neighboring charged atoms, and partially cancels the effect of charge on the atom under consideration. The form of the Madelung correction chosen here is simply q/r^2 , which is assumed to be adequate for

closed shell ions at fairly large separations.

The Hückel energy is obtained by subtracting the sum of occupied extended Hückel molecular orbital energies from the sum of one electron energies for non-interacting singly charged ions. (This latter sum remains constant at all separations due to the simple form chosen for the Madelung corrections.) The Hückel energy is assumed to contain all of the repulsive potential due to the closed shells and any covalent attraction arising from partial occupation of the K 4s orbital. To it we have added an attractive Coulomb potential, again of the simple form q^2/r^2 , which is calculated assuming unit charges at the ion nuclei.

Calculations were performed for two different sets of atomic wave functions: the commonly used Slater type orbitals (STO's), and analytic approximations to the Hartree-Fock orbitals suggested long ago by Slater⁶, which we refer to as near Hartree-Fock orbitals (NHFO's). Each NHFO consists of a fixed linear combination of a small number of STO's. The 3s and 3p states of both K and Cl were constructed exactly according to Slater's original recipe, and the K 4s state was obtained from self-consistent field results by Clementi⁷. Both sets of wave functions and the isolated ion orbital energy parameters are shown in Table 1. A more complete discussion of the use of NHFO's is given in Reference 1. The Hückel constant k_H , in the Wolfsberg-Helmholtz expression for off-diagonal matrix elements is set at 1.75 for STO's and 1.25 for NHFO's which is consistent with previous work on closed shell systems.

III. Results

The results of the various computations include overlaps, potential energies and force constants. The computed overlaps for the two sets of wave functions are compared in Figure 1. The NHFO overlaps are in general larger

and fall off more slowly with separation than the STO overlaps, with the largest difference between the two sets occurring for p-p type overlaps.

Hückel energies are shown in Figure 2. The NHFO results fall off more slowly for separations less than equilibrium and more rapidly for separations greater than equilibrium.

Total potential energies are compared with experimental data in Table II and Figure 3. The experimental curve was obtained by adding to the energy of binding terms calculated from the fourth order Taylor series expansion of the vibrational potential energy.⁸ The self-consistent field results are from augmented basis set calculations by Matcha.⁹ The shape of the potential energy curve determines the force constants, and in this respect the curve calculated with NHFO's exhibits better agreement with the experimental curve than does the curve calculated using STO's. The levels of the calculated curves, which give the binding energies, are less accurately determined, as they are extremely sensitive to the value assumed for the ionic charges in the calculation of the attractive Coulomb potential. For example, a 5% change in the assumed ion charges shifts both curves by approximately .5 ev, up to the level of the experimental curve; but this degree of accuracy in the determination of charge populations is beyond the accuracy of our calculation.

Force constants obtained from the total energy curves are given in Table III. They are calculated by a least squares fit to the function

$$E(r-r_e) = E_0 + k_e/2(r-r_e)^2 + l_e/2(r-r_e)^3 + m_e/2(r-r_e)^4,$$

where r_e is the calculated separation at the energy minimum. The NHFO results give better agreement with all three experimental force constants than do the STO results. In particular, the higher order STO force constants are much too large. This indicates that the use of NHFO's in extended Hückel calculations will give significant improvement for large displacements from equilibrium. For

our longer term objectives this is important, i.e., surface clusters, or ion motions in soft or open crystal lattices.

IV. Discussion

The charges on each ion are calculated from the extended Hückel molecular orbitals by a Mulliken population analysis. They remain within 3% of the assumed unit charge at all separations. We note, however, that this type of population analysis is inadequate for determining the distribution of overlap population between a very diffuse orbital such as the K 4s and the more tightly bound chlorine orbitals. We estimate that the calculated charges are only accurate to within several per cent, with the K 4s population consistently too small. For this reason we feel that a charge iteration procedure using calculated charges to determine orbital energy parameters and the Coulomb attractive energy would not significantly improve the potential energy.

Even without an accurate determination of the K 4s population, we can estimate the amount of K 4s participation in the molecular interaction by considering its covalent contribution to the total potential energy. This was done with a standard extended Hückel calculation, using STO's and neutral atom orbital energy parameters, with only the 4s orbital on the potassium. The resulting attractive Hückel energy is less than 10^{-3} ev for the entire range of atomic separations. This implies that the K 4s orbital is almost completely unoccupied, and tends to justify our initial assumption of unit ionic charge.

We also note that the K 4p and 3d states and the Cl 3d states all fall within a few electron volts of the K 4s and should probably be included in any precise calculation of molecular energy level ordering and splittings. But we expect their contribution to the total potential energy to be roughly the same order of magnitude as that of the K 4s, which is extremely small. Thus we feel justified in neglecting these states only because the calculation

does not give a significant population for the K 4s state. The K 4s population serves, in this respect, as an indicator of the degree of ionicity of the molecule.

V. Conclusion

The purpose of our attempts to improve conventional Hückel calculations was to take advantage of the obvious directness and highly developed computer codes which the method offers, with the objective to apply it to several solid state problems. The results reported here, with the example of K^+Cl^- , lead us to conclude that replacement of Slater orbitals by approximate Hartree-Fock orbitals (NHFO) significantly improves the agreement between theory and experiment when one considers properties other than ground state cohesive energy.

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Table I. Orbital energy parameters and wave functions used in the extended
Hückel calculations.

Orbital	Energy	STO ζ	n	NHFO ζ	coeff	
Cl ⁻ 3s	20.0	2.033	1s	14.1	.07635	
			2s	5.0	-.36329	
			3s	2.60	.50921	
			3s	1.92	.59903	
	3p	4.1	2.033	2p	6.00	.26948
				3p	2.42	-.64129
				3p	1.35	-.45897
	K ⁺	52.7	2.58	1s	15.35	.09619
				2s	5.89	-.42619
3s				3.27	.52785	
3s				2.30	.60829	
3p		31.9	2.58	2p	7.05	.29571
				3p	2.99	-.62683
				3p	1.72	-.47367
4s		8.6	.595	3s	3.95	.1237
				3s	2.61	.1089
				4s	1.26	-.3627
				4s	.75	-.6993

Table II. Calculated Hückel energies and experimental total energies (in e.v.)

r_e	NHFO		STO		EXP
	E_H	E_{TOT}	E_H	E_{TOT}	E_{TOT}
2.07	4.559	-2.40	8.393	1.43	-2.41
2.37	1.512	-4.56	2.489	-3.58	-4.05
2.57	.718	-4.88	1.051	-4.55	-4.37
2.67	.462	-4.93	.672	-4.72	-4.40
2.77	.283	-4.92	.424	-4.78	-4.38
2.97	.077	-4.77	.163	-4.69	-4.23
3.27	-.036	-4.44	.033	-4.37	-3.82

Table III. Comparison of calculated equilibrium separations, binding energies, and force constants with experiment.

	Exp	NHFO	STO
Equilibrium Separation, r_3 , Å	2.67	2.66	2.78
Binding Energy, E_0 , ev (assuming $q = 1.0$)	-4.40	4.93	-4.76
k_e	.865	.85	.90
-1_e	1.050	1.64	2.23
n_e	.775	1.52	2.99

Figure Captions

Figure 1: Computed overlaps between atomic orbitals for KCl plotted against atomic separation, R , in Angstroms. Solid line NHFO's, dashed line STO's.

Figure 2: KCl Hückel energies in electron volts plotted against atomic separation in Angstroms. Solid line calculated with NHFO's, dashed line calculated with STO's.

Figure 3: Total potential energies for KCl molecule in electron volts plotted against atomic separation in Angstroms. NHFO extended Hückel calculation with near-Hartree-Fock orbitals; STO extended Hückel calculation with Slater type orbitals; EXP experimental curve (ref. 8); SCF self consistent field calculation (Ref. 9).