Near-Minimum Basis Set SCF Calculations on HCl as a Source of Transferable Parameters

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Ab initio LCAO-MO-SCF calculations on HCl yield an optimum exponent of 1.93 for 3d Slater-type orbitals with a single radial function when best atom exponents are used for the minimum basis set orbitals of chlorine and 1.2 is used for the 1s orbital of hydrogen. Hamiltonian matrix elements and other theoretical parameters which are used in approximate MO calculations on large molecules are tabulated. One-electron properties and electron density contour maps are compared to those computed from other wave functions. The accumulation of electrons in the A-H bonds, as well as the occupation of the 3d orbitals, decreases through the isoelectronic series SiH₄, PH₃, H₂S, HCl.

Introduction

Two ab initio approaches have been used to obtain quantitative information on the extent and character of 3d orbital participation in bonds involving second-row elements, such as Si, P, S, and Cl. One such approach [1–3] has been to do LCAO-MO-SCF calculations on molecules, but, in order to be tractable, the molecules selected are usually diatomics or small polyatomics, and the basis sets are rather small, namely, the minimum basis sets of Slater-type orbitals together with the 3d orbitals of the heavy atom. These basis sets are inadequate for the purpose of obtaining Hartree-Fock descriptions of the molecules in question, but they are appropriate for obtaining theoretical parameters for transferal [1–4] to larger molecules of chemical and biological interest. By optimizing the 3d orbital exponent of a Slater-type orbital in SCF calculations on a small molecule, one has a first approximation for the value of the exponent in other bonding situations. The second theoretical approach to judging the contribution of 3d orbitals in chemical bonding is to carry out SCF calculations on the second-row atoms in
configurations which may simulate the state of the atom in a molecular environment [5–7]. These calculations are relatively simple because they avoid the evaluation of multicenter integrals.

Whereas the results of the first (molecular) approach are limited by their dependence on the basis functions, the second approach is attempting to extrapolate from atomic valence states to molecules. Yet current thinking from both approaches is that the 3d orbitals are of an appropriate size and energy for contributing to some observable properties of certain second-row molecules and that theoretical treatments of these molecules must invoke d orbital participation. Of course, calculations on molecules containing the second-row atom in a high valence state are very desirable, but such *ab initio* work is only now becoming available [8]. Full optimization of the basis sets in these calculations will lead toward the final resolution of the question of d orbital participation. The myriad of physical observables associated with the occupation of the 3d AO's in both ground and excited state molecules need not be discussed here (see, for example, [6, 9]).

The present investigation attempts to provide theoretical parameters which may be appropriate for chlorine 3d orbitals in a molecular environment. These parameters include the SCF Hamiltonian matrix elements, which may be used in the construction of Hamiltonian matrices for related, chlorine-containing molecules [4]. In addition, the optimized value of the Cl 3d exponent is reported, and a prediction [10] about its value is verified. The computed wave function of HCl is used to make interesting comparisons with existing ones for other second-row hydrides [1, 3, 11] and with published [11, 12] wave functions of HCl involving larger basis sets.

**Calculations and Energetic Results**

The near-minimum basis set SCF calculations, which were carried out with computer programs described elsewhere [13], on ground state (1Σ+) HCl at an experimental internuclear distance of 2.4087 a.u. [14] yield the results given in Tables 1 and 2. During the optimization of the 3d orbital exponent the minimum basis set exponents of Cl were held fixed at the best atom values [15] (2.0387 for 3p), and the exponent of 1.20 chosen for the H 1s orbital was judged on the basis of earlier work to be nearly optimal [1, 3]. Since the 3d exponent will depend on the other exponents, the latter were specifically chosen because of their wide usage in semiempirical MO calculations on large molecules. Similar reasoning led us to optimize the exponent of the 3d orbitals (3dz2, 3dxz, 3dyz with the molecule on the z axis) isotropically in order that a single value would be obtained for use in large asymmetric molecules. The optimum 3d exponent of 1.93 is in line with the observation [10] that the electrons in the 3d orbitals are subject to an effective nuclear charge only slightly diminished from that felt by the 3s and 3p electrons.

The total energy of HCl (Table 1) is poorer than that obtained with much larger basis sets by as much as 1 a.u., but as in the case of H2S and SiH4 [3], the near-minimum basis set gives a better energy than that obtained in the early one-center basis set calculations [12].

In studies of appropriate expressions for total energy in semiempirical MO theory, two cancellations between energy terms have been noted [16, 17]. It is