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Nuclear Repulsion Effects in Molecular Bonding

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Potential energy curves of a single electron moving in the joint Coulomb field of two fixed nuclei of equal arbitrary charge, Z, have been calculated exactly using a scaling relationship derived in an earlier paper. The resulting potential curves display some interesting features. For $Z<1$ the $2p\sigma$ "antibonding" orbital becomes "bonding", while the $1s\sigma$ potential well becomes deeper. For larger Z, the $1s\sigma$ orbital eventually becomes "antibonding" but the potential curve passes through a number of distinct intermediate stages before a purely repulsive potential is reached.

1. Introduction

In a recent paper [3], we have derived a scaling relationship for the electronic energy of a homonuclear diatomic ion. This relation has now been used to determine *exact* potential energy curves (within the usual Born-Oppenheimer approximation [2]), for the motion of an electron moving in the Coulomb field of two fixed nuclei of *arbitrary* charge. Such a system might be expected to correspond roughly to an electron in a diatomic molecule, since the remaining electrons serve (in a first approximation) to screen the nuclear field which a given electron experiences.

Some of our results are a little surprising. In particular, we find that the identification of the molecular orbitals as "bonding" and "antibonding" is not unique, but depends sensitively on the magnitude of the nuclear charges. Some of the resulting potential energy curves bear an obvious relationship to curves derived from experimental data on diatomic molecules, and may be useful in their interpretation.

2. Exact Potential Energy Curves

We consider a single electron moving in the field of two charges Z which are supposed fixed at an internuclear separation of $2R$. Then, neglecting the coupling between electronic and nuclear motions, we have for the total electronic potential energy

$$V(Z,R)=E_{\mathrm{el}}(Z,R)+\frac{Z^2}{2R} \tag{1}$$

where $E_{\mathrm{el}}(Z,R)$ is the electronic energy and $Z^2/2R$ is the Coulomb repulsion of the nuclei. Atomic units have been used throughout. If all distances are scaled so that, in particular

$$\bar{R} = ZR \tag{2}$$

we have shown previously [3] that

$$E_{\mathrm{el}}(Z, R) = Z^2 E_{\mathrm{el}}(1, \bar{R}). \tag{3}$$

Since also

$$Z^2/2R = Z^3/2\bar{R} \tag{4}$$

we have at once from Eq. (1) that

$$V(Z, R) = Z^2 V(1, \bar{R}) \tag{5}$$

where

$$V(1, \bar{R}) = E_{\mathrm{el}}(1, \bar{R}) + \frac{Z}{2\bar{R}}. \tag{6}$$

Exact values of $E_{\mathrm{el}}(1, \bar{R})$ are known from several calculations on H_2^+ [1, 5, 6, 8] for which $Z = 1$ and $\bar{R} = R$, and Eq. (6) allows us to derive exact potential energy curves for an ion of arbitrary nuclear charge Z. For convenience of comparison of the results, it is useful to consider the reduced potential $V(1, \bar{R})$ rather than $V(Z, R)$, and we do this in the following discussion.

3. Results and Discussion

Figs. 1 and 2 display the calculated potential energy curves $V(1, \bar{R})$ for the $1s\sigma$ and $2p\sigma$ states for various values of Z. They are, for H_2^+, the lowest states whose potential curves display the typical "bonding" and "antibonding" characteristics which we wish to examine as a function of the variable Z. Qualitatively similar results occur for other states as may be seen from Eq. (6).

3.1. The $1s\sigma$ State[1]

For $Z < 1$, we see that the potential well becomes deeper, the binding energy increases and the equilibrium internuclear separation decreases. A maximum binding of 0.113 a.u. occurs when Z is approximately equal to 0.5 at an actual equilibrium separation very close to 2 a.u. The corresponding binding in H_2^+ is 0.103 a.u.

For Z slightly greater than unity, the depth of the potential well decreases, together with the binding energy, while the equilibrium separation increases slightly. In addition, we have the first signs of a potential barrier at larger separations. As Z increases, the repulsive barrier increases in height, while the minimum of the potential well rises steadily above the dissociation limit, so that we have "quasi bound" vibrational levels.

We note that this type of potential barrier has been observed in diatomic spectra and has been attributed generally to the centrifugal potential associated with nuclear rotational motion [7]. A potential well lying above the dissociation limit has usually been associated with one of the mechanisms of pre-dissociation [4].

For Z greater than about 1.44, the $1s\sigma$ potential curve is everywhere repulsive.

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[1] Results somewhat similar to ours in section 3.1 have been obtained by Feinberg and Hass in their study of model two-electron diatomic molecules [Theoret. chim. Acta (Berl.) 7, 290 (1967)].

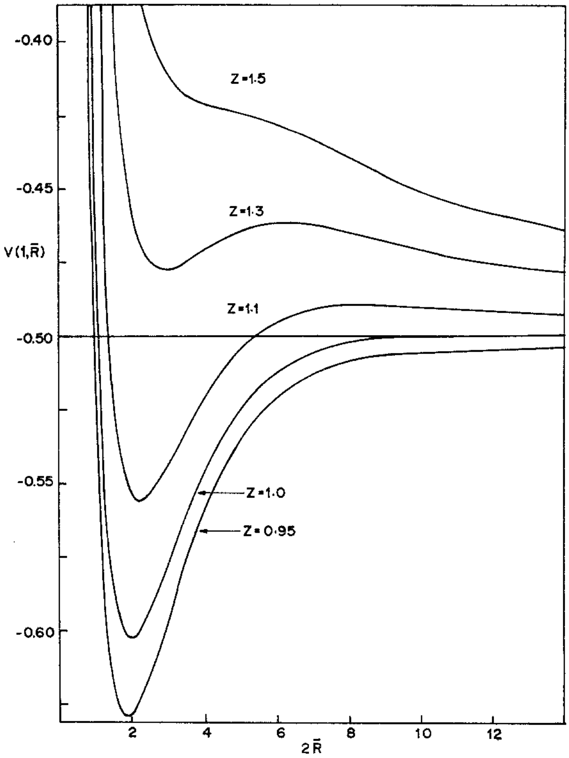

Fig. 1. Reduced potential energy curves for the $1s\sigma$ state

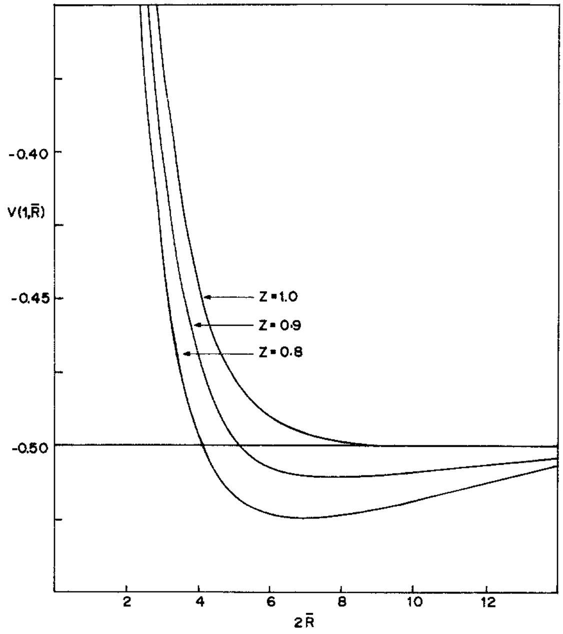

Fig. 2. Reduced potential energy curves for the $2p\sigma$ state

3.2. The $2p\sigma$ State

For $Z \geqq 1$, the potential is everywhere repulsive, but for slightly smaller values of Z, there is a very shallow potential well at large internuclear separations. Thus, the contribution to the binding from an electron in such a molecular orbital will be very small although it may be comparable with the contribution from a higher "bonding" orbital (for example, the $2s\sigma$ orbital). A maximum binding of 0.0209 a.u. occurs when Z is approximately equal to 0.65 at an equilibrium separation close to 4.6 a.u.

We note in conclusion that similar effects have been found for excited π and δ states of the single electron ion, though they are less marked than for the cases treated here.

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