Variational Calculation of the 1sσ Orbital in Quasi-Molecular Systems

D.H. Jakuballa

Physik-Department, Technische Universität München, Garching, Federal Republic of Germany

Received October 7, Revised Version November 24, 1977

We describe a simple analytical model for the ground state energy of an electron in a two-center potential. An effective charge \( Z(R) \) is derived which corresponds to the monopole approximation of this potential. As an example, we study the \((H, H)\) and \((Br, Zr)\) systems.

1. Introduction

The theory of K-shell ionization in adiabatic heavy-ion collisions requires knowledge of the electronic energy \( E(R) \) and wave function \( \psi(R) \) as a function of the separation \( R \) between projectile and target nucleus. The application of an exact two-center calculation \[1\] is, however, very cumbersome. Therefore several approximations have been introduced such as the replacement of \( E(R) \) and \( \psi(R) \) by their values in the united atom limit \((R = 0)\) \[2\] or at the distance \( R_d \) of closest approach \[3\]. Recently a perturbative expansion of the binding energy at \( R_a \) combined with a variational calculation where the extension \( x^\ast \) of the \( ls \) wave function is optimized, had also been performed \[4\].

In this paper we derive an approximation for \( E(R) \) by taking a spherically symmetric wave function \( \psi_s(R) \) with the origin at a distance \( x \) from the target nucleus in the direction of \( R \), and by optimizing \( k \) and \( x \) for fixed \( R \). In Section 2 we calculate the ground state energy non-relativistically and give in Section 3 an extension to the relativistic case. In Section 4 follows a discussion of the functional dependence of \( E \), \( k \) and \( x \). As an example the systems \((H, H)\) and \((Br, Zr)\) are considered.

2. Charge Cloud Model in the Nonrelativistic Case

There are quite a few approaches to the determination of the energy of an electron in a diatomic system by a variational calculation, mainly applied to \((H, H)\) or other light nuclei. They range from a simple semiclassical model where the electron is described by a homogeneously charged sphere \[5\] to very refined calculations which use spheroidal wave functions for the electron. These functions contain one \[6\] or two \[7\] variational parameters which correspond to a variable nuclear charge or to a variable location and extension of the electron distribution respectively.

The model described below does not claim to give an optimal fit to the energy of the electron. But its simplicity helps to extract the physical significance of the introduced parameters. It is not confined to symmetric systems and is meant to be applied in slow collision processes.

An electron in the field of projectile and target nucleus with charge \( Z_1 \) and \( Z_2 \) respectively is described by the Hamiltonian

\[
H = -\frac{\hbar^2}{2m} \Delta - \frac{Z_1 e^2}{|r-R-x|} - \frac{Z_2 e^2}{|r-x|}.
\]

The coordinates are shown in Figure 1. The expectation value of \( H \) is calculated with the \( ls \) wave function

\[
\psi_s = \pi^{-1/2} \kappa^{3/2} \exp(-\kappa r)
\]

and depends on the parameters \( \kappa \) and \( x \):

\[
E = \frac{\hbar^2}{2m} \kappa^2 \left[1/(R-x) - e^{-2\kappa(R-x)}(1/(R-x)+\kappa)\right] - \frac{Z_1 e^2}{1/(R-x)} \left[1/(x) - e^{-2\kappa X(1/(x)+\kappa)}\right].
\]

For \( Z_1 = Z_2 \) it is symmetric with respect to the interchange of \( x \) and \( R-x \). \( \kappa \) and \( x \) are obtained from
minimizing the energy. The limiting cases \( R = 0 \) and \( R = \infty \) coincide with the exact solution. From \( \partial E / \partial x = 0 \) one finds \( x = R Z_1 / (Z_1 + Z_2) \) for \( R \to 0 \) which is the center of charge, and \( x = 0 \) for \( R = \infty \) which yields the boundary condition for the \( 1s \sigma \) energy when \( Z_2 > Z_1 \). The second equation \( \partial E / \partial \kappa = 0 \) leads to \( \kappa = (Z_1 + Z_2) / a_0 \) for \( R = 0 \) and \( \kappa = Z_2 / a_0 \) for \( R = \infty \), where \( a_0 \) is the Bohr radius \( \hbar^2 / m e^2 \).

3. Extension to the Relativistic Case

An application of the variational principle to the Dirac equation meets the difficulty that the Dirac operator has no lower boundary [8]. This can lead to an overestimate of the binding energy due to the coupling of the negative continuum states. In the region with \((Z_1 + Z_2) \alpha \geq 1 \) \( (\alpha = e^2 / \hbar c) \) a variational calculation of the ground state energy is no longer reasonable. For charges where the point nuclei are still a good approximation one can use the wave function

\[
\psi = N \exp(-\kappa r) r^{\gamma - 1} \begin{cases} \lambda \\ -\mu \end{cases} \quad (3.1)
\]

where \( N \) is the normalization constant and \( \kappa, \lambda \) and \( \mu \) are variational parameters. In the case of an atom \( (R = 0 \) or \( \infty) \) this leads to the exact Dirac \( 1s \) energy and wave function.

The calculation is, however, much simplified if we use the Schrödinger operator (2.1) with (2.2) but replace the kinetic energy in (2.3) by the relativistic expression

\[
E_{\text{kin}} = (m^2 c^4 + \hbar^2 \kappa^2 c^2) / 2 - m c^2. \quad (3.2)
\]

This leads also to the Dirac \( 1s \) energy in the atomic case, with \( \kappa \) given by \( Z / a_0 (1 - (Z \alpha)^2)^{-1/2} \), \((Z = Z_2 \) or \( Z_1 + Z_2)\).

4. Results and Discussion

In Figure 2 the \( 1s \sigma \) energy obtained by minimizing (2.3) is compared to the numerical solution of the two-center problem. For relativistic systems the replacement (3.2) is used in order to obtain the correct energies in the limiting cases \( R = 0 \) and \( R = \infty \). Examples are given for \((H, H) \) [9] and \((Br, Zr) \) [10]. We obtain a fairly good agreement, the deviations at \( R/a_2 \sim 2 \) \((a_2 = a_0 / Z_2)\) resulting from the deformation of the electron distribution which is not included in (2.2).

Figure 3 shows the monopole polarization \( x \) of the electron cloud as a function of the nuclear separation \( R \). In the case of symmetric systems we find a "phase transition" for \( R/a_2 \sim 1 \) which is correlated to the symmetry breaking of the wave function [11]. It is due to the classical description of the location of the electron. In a quantum mechanical treatment with symmetrized wave functions the location can not be observed.

It should be mentioned that in the nonrelativistic case the quantities \( E / E_2 \) \((E_2 = -Z_2 e^2 / 2a_2)\), \( x / R \) and \( \kappa a_2 \) are only functions of \( R / a_2 \) and \( Z_1 / Z_2 \).

The parameter \( \kappa \) which describes the extension of the electron cloud, can be related to an effective nuclear charge \( Z(R) \). It is defined by \( Z = \kappa a_0 \) in the nonrelativistic case and by \( Z = (x^2 + (\kappa a_0)^{-2})^{-1/2} \) in the relativistic case and changes from \( Z_1 + Z_2 \) to \( Z_2 \) when \( R \) goes from zero to infinity. By means of \( Z(R) \) one may