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Variational Calculation of the $1s\sigma$ Orbital in Quasi-Molecular Systems

D.H. Jakubaßa*
Physik-Department, Technische Universität München,
Garching, Federal Republic of Germany

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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_d combined with a variational calculation where the extension κ^{-1} of the $1s$ 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 $\mathbf{R}$, and by optimizing κ 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, κ 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

$$H=-\frac{\hbar^2}{2m}\Delta-\frac{Z_1 e^2}{|\mathbf{r}-\mathbf{R}-\mathbf{x}|}-\frac{Z_2 e^2}{|\mathbf{r}-\mathbf{x}|}. \tag{2.1}$$

The coordinates are shown in Figure 1. The expectation value of H is calculated with the $1s$ wave function

$$\psi_s=\pi^{-1/2}\kappa^{3/2}\exp(-\kappa r) \tag{2.2}$$

and depends on the parameters κ and x:

$$\begin{aligned}E=&\hbar^2\kappa^2/2m\\&-Z_1 e^2[1/(R-x)-e^{-2\kappa(R-x)}(1/(R-x)+\kappa)]\\&-Z_2 e^2[1/x-e^{-2\kappa x}(1/x+\kappa)].\end{aligned} \tag{2.3}$$

For $Z_1=Z_2$ it is symmetric with respect to the interchange of x and $R-x$. κ and x are obtained from

* And GSI, Darmstadt

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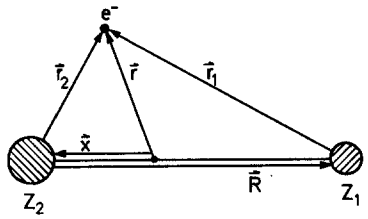

Fig. 1. Coordinate system for an electron in the field of projectile and target nucleus

minimizing the energy. The limiting cases $R=0$ and $R=\infty$ coincide with the exact solution. From $\partial E/\partial x=0$ one finds $x=RZ_1/(Z_1+Z_2)$ 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 $\hbar^2/me^2$.

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 $(Z_1+Z_2)\alpha\gtrsim 1$ ($\alpha=e^2/\hbar c$) 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

$$\psi_s=N\exp(-\kappa r)r^{\gamma-1}\begin{cases}\lambda\\-\mu\end{cases}$$

with $\gamma=(1-(\hbar\kappa/mc)^2)^{1/2}$ (3.1)

where N is the normalization constant and κ, λ and μ are variational parameters. In the case of an atom ($R=0$ or ∞) 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

$$E_{\text{kin}}=(m^2c^4+\hbar^2\kappa^2c^2)^{1/2}-mc^2. \quad (3.2)$$

This leads also to the Dirac $1s$ energy in the atomic case, with κ 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).

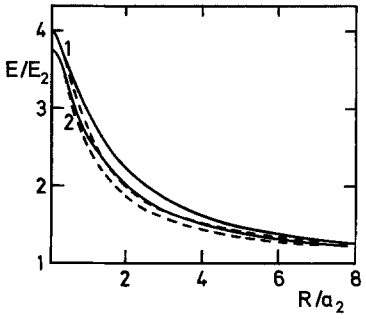

Fig. 2. $1s\sigma$ energy as a function of the internuclear distance. 1 refers to the (H, H) system and 2 to the (Br, Zr) system. The solid lines are two-center calculations and the dashed lines originate from the variational model

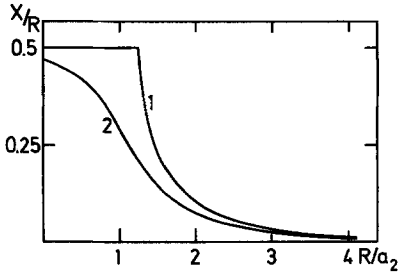

Fig. 3. Center of the electron distribution for the $1s\sigma$ state as a function of the internuclear distance. 1 refers to the (H, H) system and 2 to the (Br, Zr) system

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 ($E_2=-Z_2e^2/2a_2$), x/R and κa_2 are only functions of R/a_2 and Z_1/Z_2.

The parameter κ 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 $Z=(\alpha^2+(\kappa a_0)^{-2})^{-1/2}$ 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

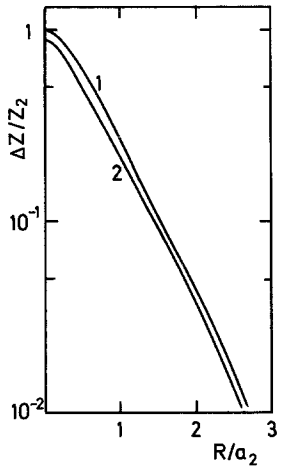

Fig. 4. Shift of the effective nuclear charge as a function of the internuclear distance. 1 refers to the (H, H) system and 2 to the (Br, Zr) system

introduce an effective potential $-Z(R)e^2/r$ by which the two-center Coulomb field can be replaced in the context with the monopole approximation [12] in the K-shell ionization theory. In the adiabatic perturbation theory the transition operator is the time derivative of this potential, i.e. proportional to $(dZ(R)/dR)\,dR/dt$. We find an exponential decay of the shift $\Delta Z(R)=Z-Z_2$ with R as can be seen in Figure 4. Thus, when taking the R-dependent energy and wave functions from our variational model we obtain a consistent description within the monopole approximation.

To summarize, we have described a method for the calculation of the ground state energy and wave function of quasimolecular systems, intended to be applied within the monopole approximation for K-shell ionization. We have shown that by a two-parameter variational calculation valid for all systems with $(Z_1+Z_2)\alpha<1$ the $1s\sigma$ energy is reproduced up to 10%. We have derived an effective charge and thus related some properties of a two-center potential to those of a monopole potential.

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Doris H. Jakubaßa
Physik-Department
Technische Universität München
Theoretische Teilinstitut
D-8046 Garching, Reaktorgelände
Federal Republic of Germany