

New approach for approximating the continuum wave function by Gaussian basis set

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The use of Gaussian type Orbitals (GTOs) to describe atomic and molecular states has become a fundamental tool in quantum chemistry because of the computational advantages they offer [1]. There are currently many GTO bases and programs for use in calculations involving molecular structure bound states. They are, however, very few methods for generating GTOs for continuum states and few programs that address problems involving these states as may be the case of ionization. These methods approximate the oscillating radial wave functions [2] using a set of gaussians. Thus for obtain convergence they need a large set of basis functions.

In this work we will use a new way of calculating continuous wave functions.

The continuum wave function can be written as the product of a plane wave by a distortion produced by the central potential:

$$\phi(r) = \frac{e^{ik \cdot r}}{(2\pi)^{3/2}} D(k, r) \quad (1)$$

We only expand the distorting factor in a series of spherical function of the form

Thus,
$$D(\mathbf{k}, \mathbf{r}) = \sum_{l,m} D_l(k, r) Y_l^m(\hat{\mathbf{k}}) Y_l^{m*}(\hat{\mathbf{r}})$$
 the plane wave in (1) representing the kinematical characteristic of the continuum is left intact.

With this method we obtain a more accurate and rapid approximation since avoid having to bring strongly oscillating function as being the plane waves. We note that distortion $D_l(k, r)$ has a relatively smooth behaviour, allowing rapid convergence in partial waves. In a previous work [3] we had used this approach to the Coulomb case. We got a quick convergence in

partial waves and we could approximate the smooth distortions in Gaussians orbital very efficiently. And also, the analytical methods for evaluating gaussian integrals are maintained.

In this work we extend the method to any radial potential. So we can describe any atom by a central potential as a OPM [4]. We analyse the properties of the solutions obtained, their asymptotic forms, and how to extract relevant information from the collision process from these functions and their link with traditional development. By some examples show the advantages and disadvantages of this method compared to usual.

As an example we will use these functions to calculate ionization cross sections of the hydrogen molecule using the Born approximation. To describe the states, bound and continuum we used gaussians basis.

References

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