

# From Chemical Bonding to Confinement due to Nonadiabatic Processes by the Enhancement of Quantum Fluctuations

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The physical nature of chemical bonding has been studied in the adiabatic approximation in which only electronic motion contributes to the formation of covalent bonds. Although this approximation may well apply to most realistic molecules and solids, a more comprehensive understanding of chemical bonding will be obtained by investigating the roles of quantum fluctuations of nuclei in the bond formation.

We have commenced such an investigation by considering a hydrogen-like molecule,  $(M^+M^+m^-m^-)$ , composed of two unit-positive charge particles ('protons') with mass  $M$  and two electrons with mass  $m$ . The mass ratio  $m/M$  is changed continuously from zero (the adiabatic limit) to unity (the limit of dipositronium), covering the issue of a biexciton or a bound complex of two electrons and two holes in between. We have employed the diffusion Monte Carlo (DMC) simulations at zero temperature in order to evaluate the exact values for various ground-state properties such as the total energy  $E_0$  and the average separation of 'protons' (or the bond length), together with the corresponding ones in the adiabatic approximation.

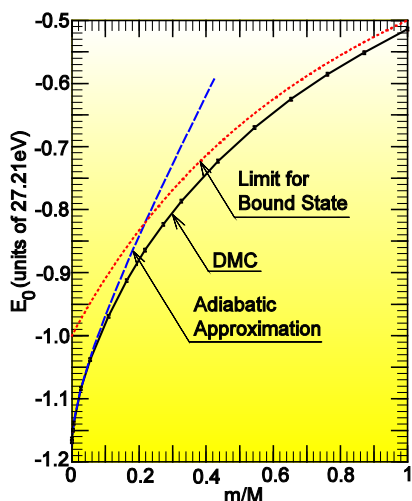


Fig. 1. Ground-state energy of a hydrogen-like molecule  $(M^+M^+m^-m^-)$  in both DMC and the adiabatic approximation as a function of the mass ratio  $m/M$ .

In Fig. 1, the calculated result for  $E_0$  in DMC is shown as a function of  $m/M$  by the solid curve. The obtained  $E_0$  increases monotonically with increasing  $m/M$ , but it is always smaller than the upper limit of the energy for the existence of a bound state of this four-body problem (the dotted curve), namely,  $E_0 = -M/(m+M)$ . The adiabatic approximation provides a very accurate value for  $E_0$  with relative errors less than only 1% as long as  $m/M$  is smaller than 0.1, convincing us that the binding mechanism for this molecule in this range of  $m/M$  is nothing but the chemical bonding in the usual argument [1].

The decrease of the binding energy with increasing  $m/M$  is associated with the rapid increase of the bond length as shown in Fig. 2. Thus the vibrons or the zero-point quantum fluctuations of 'protons' are found to hamper this chemical bonding by weakening the binding energy and widening the bond length.

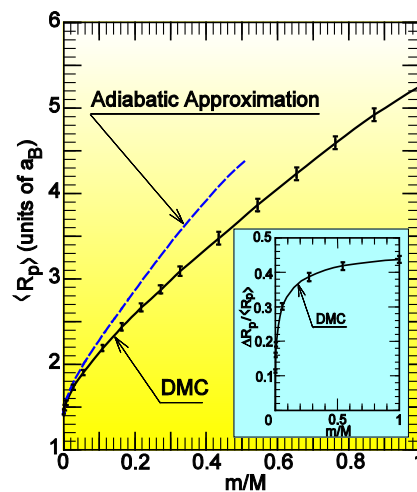


Fig. 2. Average distance between two 'protons'  $\langle R_p \rangle$  in units of the Bohr radius as a function of  $m/M$ . The inset shows the relative variation  $\Delta R_p / \langle R_p \rangle$ .

For  $m/M$  larger than about 0.2, the adiabatic approximation becomes too crude to support any bound states in the system. Concomitant with this result for  $E_0$ , the variation of 'proton' positions is as large as the average separation of two 'protons'. This implies that proton motion has changed its character with the increase of  $m/M$ ; at  $m/M < 1$ , 'protons' are localized and separated to each other by the bond length, while for  $m/M$  larger than about 0.2, they overlap in the whole molecule in just the same way as electrons.

Since the adiabatic potential cannot afford an enough attractive energy to bind 'protons' for  $m/M > 0.2$ , the existence of a bound state (or the confinement of this four-body system) as demonstrated by DMC suggests that nonadiabatic processes or the effects due to retardation of electron response to 'proton' motion should play a crucial role in the binding mechanism for  $m/M$  in this region [2].

Finally we note that the parameter  $m/M$  controls the two competing effects on the binding mechanism; one is to weaken the binding force through enhancing quantum fluctuations and the other is to strengthen it through promoting nonadiabatic processes. The crossover takes place at  $m/M$  around 0.2.

## References

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- [2] Y. Takada and T. Cui, *J. Phys. Soc. Jpn.* **72**, 2671 (2003).

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