

Electron Wave Packet Modeling of Chemical Bonding

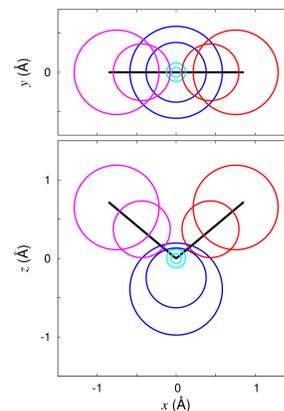
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Following our recent development of nuclear wave packet (WP) molecular dynamics simulation of liquid water [1], we have been extending the method to many fermion systems [2] with aim to combine nuclear and electron WP methods in a compact and consistent manner. An essential part to this end is a proper account of the antisymmetry of fermion wave functions, for which we deploy the valence-bond (VB) theory that fits better with the localized WP picture than does the molecular orbital framework. In contrast with the conventional VB theories that employ frozen atomic orbitals (AOs) clamped on nuclear positions, our electron WPs can float and breath; namely, each electron is described by a single (minimal) spherical gaussian WP with freedom to move in space (float) and to change its width (breath). Despite its simplicity, this floating and breathing minimal electron WP with VB coupling has been found to give reasonably accurate ground state potential energy surfaces of H₂, LiH, BeH₂, CH₂ (Figure) and H₂O. Particularly interesting aspect was its capability to describe the cases in which conventional methods require nodal basis functions such as p-type AOs. This comes from the flexibility of the floating WPs to describe deformation of electron density, or polarization, in the ground state total wave functions that are generally nodeless. Roughly, the static correlation is accounted for by the floating WP and the VB coupling, while the dynamic correlation is by the breathing WP.

The method is now being extended toward electron-nuclear dynamic simulations. The WP description has a versatility to describe more complicated wave functions with quantum phase factors by invoking the coherent state path integrals with Monte Carlo sampling. Excited states will be studied by the dynamical response theory.



- [1] Hyeon-Deuk, K., Ando, K. *J. Chem. Phys.* 131:064501, 2009; *ibid.* 132:164507, 2010; Ono, J., Hyeon-Deuk, K., Ando, K. *Int. J. Quant. Chem.* 113:356, 2013; Ono, J., Ando, K. *J. Chem. Phys.* 137:174503, 2012.
- [2] Ando, K. *Bull. Chem. Soc. Jpn.* 82:975, 2009; *Chem. Phys. Lett.* 523:134, 2012; Hyeon-Deuk, K., Ando, K. *ibid.* 532:124, 2012.