

# Quantum chemistry with accurate solutions of the Schrödinger equation

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The theory that solves the Schrödinger equation exactly is a goal and a starting point of the quantum chemistry. The free complete-element function (FC) theory is such a theory born in 2004. The theory has been extended since then and its accuracy, reliability, and high performance have been confirmed. It predicts the energies and properties of atoms and molecules in high accuracy that is comparable to or even better than the experimental values. To develop this theory for general use in quantum chemistry is our current subject.

The equation that gives the solution of the Schrödinger equation with the variational method is the scaled Schrödinger equation  $g(H - E)\Psi = 0$ [1], where  $g(r)$  is the scaling function that is always positive and its correct function behaves as  $g = r + O(r^2)$  near  $r = 0$  and  $g \rightarrow 1$  when  $r \rightarrow \infty$ . As such correct function, the following five are known[2].

$$1 - \exp(-\gamma r), Ei(-\gamma_1 r - \gamma_2) - Ei(-\gamma_2), r/(r + 1/a), \arctan(\gamma r), \tanh(\gamma r) \quad (1)$$

The function  $r$ , frequently used, does not satisfy the above correct behaviors. Actually,[2] the correct functions give usually better results than the function  $r$  that has been used frequently. For general molecules, the integrals for  $g_{ij}$  is difficult. So, the variational parameters are optimized by the sampling method that uses the Schrödinger equation itself as a deterministic equation[3]. It is called local Schrödinger equation (LSE) method[3]. As sampling method, the Metropolis method is popular, but because it is a stochastic method, it usually includes the error caused by the randomness. So, we introduced the inverse transformation (direct) method using the integrable initial functions of the FC theory[4]. With this method, we could obtain highly accurate potential energy curves for the lower nine valence states of the  $\text{Li}_2$  molecule[5]. They agreed in the absolute energy to the experimental RKR potentials within the difference of 0.058 kcal/mol from the experimental values. The chemical reaction dynamics of the ground and excited states of this molecule is governed by these potential curves, and therefore, the FC theory is able to describe the reaction dynamics of this molecule almost completely. We are also developing the FC theory for the BO treatment.

Since the FC theory is an exact theory, it can predict not only the energies, but also the properties observed by many different experiments highly accurately. For example, for the  $^2S$  and  $^2P$  states of the Li atom, we calculated the spin densities at the nucleus that are widely observed by the ESR experiments, electron-nuclear and electron-electron cusp values, etc. For example, for the spin densities of the  $^2S$  and  $^2P$  states, the experimentally observed values were 0.2313 and -0.01693, respectively, while the calculated values with the FC theory were 0.2311 and -0.01693, respectively, while the calculated values with the FC theory were 0.2311 and -0.01704, respectively, which are almost complete agreement with the experimental values.

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