Iterative Complement (IC) method for solving the Schrödinger equation of Atoms and Molecules

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The Iterative Complement (IC) method,[1,2] was presented to solve the Schrödinger equations of atoms and molecules. In this method, the Hamiltonian of a system is divided into N_D parts, and the wave function is defined in the recurrence relation

$$\psi_{n+1} = \left[1 + \sum_{I=1}^{N_D} C_{I,n} g(H_I - E_{I,n}) \right] \psi_n$$

where $E_{I,n}$ is defined by $\langle \psi_n | g(H_I - E_{I,n}) | \psi_n \rangle = 0$. The corresponding set of secular equations is solved to determine the N_D variables. Compared with the Free Complement (FC) method,[3] the IC method has the merit that the total number of variables is much smaller. Moreover, the dimension of the matrix does not increase as the computation order grows. So it is essentially a diagonalization-free method and is very suitable to super-parallel computers, though the IC method converges more slowly than the FC method.

In order to increase the convergence speed, we have developed the method which re-optimizes the lower order coefficients with the existence of the higher order variables. The interaction among complement functions from different orders is explicitly taken into account. We have formulated this procedure in the iterative manner. Accordingly the secular equations are solved iteratively and the convergence of the IC method is considerably improved.

To further increase the convergence, we introduce more freedom to the IC wave function. We combine the calculation of different levels together, and then all the independent operators are collected to generate complement functions. The number of variables in each iteration is larger compared to the original IC method because the Hamiltonian is divided to the maximum partition, so that the IC wave function is more relaxed. While the dimension of matrix in each iteration step is still constant, so the computational effort for the diagonalization does not increase as the order grows.

Table I: Energies of Original IC method, relaxed IC method, extended IC method, and FC method. Helium Atom

Order	Original IC (N_D=1)	relaxed IC (N_D=1)	extended-IC2			FC	
			M_N	Total number of variables	Energy	M_N	Energy
1	−2.8983832	−2.8998717				6	−2.9015710
2	−2.9009105	−2.9024739	26	26	−2.9036966	26	−2.9036966
3	−2.9015583	−2.9032702				74	−2.9037224
4	−2.9018020	−2.9035185	57	83	−2.9037232	159	−2.9037240
5	−2.9019321	−2.9036142				291	−2.9037243
6	−2.9020136	−2.9036580	57	140	−2.9037241	481	−2.9037243
7	−2.9020695	−2.9036809				738	−2.9037243
8	−2.9021102	−2.9036944	57	197	−2.9037242	1074	−2.9037243
Exact Value			−2.903724377				

The IC method with variational principle is demonstrated to be very effective, however, the analytical integrals are not always feasible. So the Local Schrödinger equation (LSE) method,[4] is combined with the IC method to solve the Schrödinger equation of general atoms and molecules. Moreover, The combination of LSE with the IC method is especially suitable for parallel computation, because the IC method avoided large dimensional matrix-matrix multiplication, and the sampling itself is a series of independent calculation which can be paralleled effectively.

In contrast to the FC method, the IC method is essentially a single state theory, so the excited states are not obtained simultaneously with the ground state. So the IC-configuration interaction (CI) method is presented to calculate excited states from the IC ground state wave function. The frame work of the IC-CI method is similar to the SAC-CI method proposed in 1978. The IC-CI SD and IC-CI general approaches are formulated.[2,5]

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