Solving the Schrödinger equation of a few electron atoms and molecules with the free ICI VP method

Hiroyuki Nakashima and Hiroshi Nakatsuji

(http://qcri.or.jp/)

Quantum Chemistry Research Institute (QCRI), Kyoto, Japan

CREST, Japan Science and Technology Agency (JST), Japan

Graduate School of Engineering, Kyoto University, Kyoto, Japan

Schrödinger equation (SE) is the most important principle of chemical science. For solving the SE of general atoms and molecules, we proposed the free ICI (iterative-complement-interaction) method [1] and applied it to various systems. Here, we show some of the results obtained by combining it with the variational principle (VP). The free ICI method itself is applicable to any systems when its Hamiltonian is explicitly defined and can be extended for solving the relativistic Dirac-Coulomb equation [2].

1. He to B atoms: As previously reported, we performed the calculations of helium atom in fixed nucleus approximation ($^{\infty}$He) and gave the best variational energy of **-2.903 724 377 034 119 598 311 159 245 194 404 446 696 9**05 37 a.u. with 40 digits accuracy [3]. The same calculations were performed up to the five-electron B atom and molecules, which also showed very good convergence to the exact solutions.

2. Non Born-Oppenheimer calculations: We included nuclear motion as well as electron motion in the Hamiltonian and solved the SE. This represents "the nonrelativistic limit". For helium, the Hamiltonian contains the reduced mass: μ and the mass polarization term: $1/m_N \cdot \nabla_1 \cdot \nabla_2$. With the mass of nucleus (^{4}He) of m_N=7294. 299 536 5 (a.u.), the energy correct at least to 40 digits is **-2.903 304 557 729 580 294 733 816 943 892 697 752 659 27**3 96 a.u. We have also calculated the energies of the helium iso-electronic atoms.

3. Excited states: The free ICI method is not limited to the ground state but is easily applicable to the excited states. Table I shows the excitation energies of helium atom with nucleus in motion (non-BO approximation). Compared with the experimental values, the differences were within 10^{-5} a.u. except for the lowest excited state and they reflect the physical effects not contained in the SE (QED and relativistic effects).

4. Hydrogen and helium atoms in strong magnetic fields: The free ICI method was applied to hydrogen and helium atoms in strong magnetic fields. Even in extremely strong magnetic fields like that existing in the neutron star (10^{10}-10^{13} G), the solution could be obtained quite stably. The energy of hydrogen atom in magnetic fields of B=1 (a.u.) was over 100 digits in accuracy!! Our theory would be a powerful tool to study the spectroscopy from astrophysical objects and determine the magnetic field strength of them.

Recently, we developed the Local Schrödinger equation (LSE) method [4] without doing analytic integrations. Therefore, we can apply the ICI methodology to general atoms and molecules without doing any integration.

Table I. Excitation energies of helium atom of 1sNs states for singlet.

N	Free ICI (a.u.)	Exptl. (a.u.)	[Theory]-[Exptl.]
2	0.757 625 970 149	0.757 615 762 6	**0.0000** 102 075
3	0.842 315 475 381	0.842 306 138 8	**0.00000** 933 66
4	0.869 996 740 248	0.869 988 158 2	**0.00000** 858 21
5	0.882 404 831 556	0.882 396 351 2	**0.00000** 848 03
6	0.889 017 646 545	0.889 009 221 2	**0.00000** 842 53
7	0.892 954 413 278	0.892 946 017 0	**0.00000** 839 63
8	0.895 486 211 526	0.895 477 830 3	**0.00000** 838 12
9	0.897 210 038 953	0.897 201 55	**0.00000** 848 69
10	0.898 436 428 854	0.898 428 07	**0.00000** 835 69
11	0.899 339 879 169	0.899 331 46	**0.00000** 842 26
12	0.900 024 574 124	0.900 016 00	**0.00000** 857 38
13	0.900 555 835 611	0.900 547 72	**0.00000** 811 09
14	0.900 976 305 419	0.900 968 23	**0.00000** 807 66
15	0.901 314 778 506	0.901 306 67	**0.00000** 810 51

References: [1] H. Nakatsuji, *J. Chem. Phys.* **113**, 2949 (2000)., H. Nakatsuji, *Phys. Rev. Lett.* **93**, 030403, (2004)., H. Nakatsuji, *Phys. Rev. A* **72**, 062110 (2005). [2] H. Nakatsuji and H. Nakashima, *Phys. Rev. Lett.* **95**, 050407, (2005). [3] H. Nakashima and H. Nakatsuji, *J. Chem. Phys.* in press. [4] H. Nakatsuij, H. Nakashima, Y. Kurokawa, A. Ishikawa, *Phys. Rev. Lett.* in press.