Variational principles for critical parameters and ionization energies of quantum systems

Alexei Sergeev and Sabre Kais

Purdue University, Department of Chemistry
West Lafayette, IN 47906

Non−traditional applications of variational methods were proposed both for critical parameters (when the energy crosses the ionization threshold) and for the energy below and above ionization threshold.

If the critical parameter enters the Schrodinger equation linearly, then the equation for critical parameters can be considered as a generalized eigenvalue equation with a non−trivial weight operator. Consider, for example, a two−electron atom

$$H = p_1^2/2 + p_2^2/2 - Z/r_1 - Z/r_2 + 1/r_{12}$$

with a charge Z treated as a continuous parameter.

After scaling transformation $r \rightarrow Z\,r$, the Schrodinger equation for the state that reaches the border of continuum, $H\,\psi = -Z_c^2/2\,\psi$, can be rewritten as

$$(p_1^2/2 + p_2^2/2 - 1/r_1 - 1/r_2 + 1/2)\psi = \lambda\,(1/r_{12})\,\psi$$

where $\lambda = -1/Z_c$ is a generalized eigenvalue. Then, the expectation value

$$\langle p_1^2/2 + p_2^2/2 - 1/r_1 - 1/r_2 + 1/2\rangle \,/\, \langle 1/r_{12}\rangle$$

gives an upper bound for λ and correspondingly an upper bound for the critical charge Z_c:

N	$-\lambda$	$-\lambda$ (D=5)
0	1.04849	0.9700
1	1.09077	0.9993
2	1.09489	1.0028
3	1.09713	1.0046
4	1.09736	1.00486
	1.09766 (exact)	1.00524 (exact)

In the above example, N is the size of Hylleraas basis set. Two nonlinear parameters (exponential factors a_1, a_2) entering the trial function were optimized. Note that five−dimensional atom (D=5) in its ground state is equivalent to the excited $2p^2\,{}^3P$ state of the 3−dimensional atom.

Accelerating of convergence by Pade approximants gives very accurate results:

N	$-\lambda$	$-\lambda$ (D=5)	$-\lambda$ (D=7)
0	1.017		0.934
2	1.095	1.003	0.966
4	1.0974	1.00476	0.9686
6	1.09764	1.00518	0.9694
8	1.097658	1.00522	0.9701
10	1.0976605	1.005243	
	1.09766079	1.00524 (exact)	

Above, nonlinear variational parameters (a_1, a_2) are (0.4, 1), (0.2, 0.5), and (0.11, 1/3) for D = 3, 5, and 7 respectively.

For the 7−dimensional atom, the critical charge is probably one, but the convergence is slower.

The critical charges were found for two−electron atoms subject to external magnetic field as a function of magnetic field strength, see Figure 1.

For variational calculations, we used "spherical" basis set, i. e. products of spherically−symmetric functions and spherical harmonics. Satisfactory accuracy was obtained for weak fields less than 0.2 a. u. ($4.7 \cdot 10^4$ T). In addition, we used alternative approach based on large−dimensional analysis.

Proposed variational principle is optimized in order to give accurate estimation of the critical parameter itself rather than the energy.

For ionization energies, an ordinary variational principle for the energy functional was used, but with allowance of complex variational parameters. Above the ionization threshold, a minimum of the energy functional turnes into a complex stationary point. It means that the variational method produces complex energy that approximates position (real part) and half width (imaginary part) of the corresponding quasi−stationary state. We calculated variational energies of few−electron atoms as a function of charge of the nucleous using simple trial functions in the form of a product of exponents (including permutations).

Figure 2 shows results for the ground state of two−electron ions. A simple trial function $\exp(-a_1\ r_1\ -a_2\ r_2) + \exp(-a_2\ r_1\ -a_1\ r_2)$ with two variational parameters was used. Solid and broken lines are real and imaginary parts of the energy respectively. Red lines is the result obtained by summation of the $1/Z$−expansion.

Figure 3 shows similar results for the lowest triplet state of two−electron ions (with antisymmetric wavefunction).

Note the different behavior near the critical charge for these states. For the ground state (Figure 2), energy crosses the ionization border with a non−zero derivative that is equivalent to existance of a bound state at the critical point $Z=Z_c$. For the triplet state (Figure 3), energy approaches the ionization border with a zero derivative, and one of the exponential factors (a_1, a_2) tends to zero. It means that the wave function is no more integrable at $Z=Z_c$, and transformation to unbound state at the critical point is "continuous". The latter behavior resembles the second−order phase transition in statistical physics. Our simple variational calculation gives qualitatively correct behavior near the critical charge and provides an estimate of the energy of the quasistationary state.

Similar variational calculations are in progress for atoms with more than two electrons. Our results for the ground state of three−electron (lithium−like) and four−electron (beryllium−like) atoms are displayed on Figures 4 and 5. The critical behavior for lithium isoelectronic series ("second−order phase transition") is in agreement with a recent result of Pablo Serra et al. (Phys. Rev. Lett., in press), while the critical behavior near $Z=Z_C$ for beryllium isoelectronic series ("first−order phase transition") is qualitatively the same as for the ground state of helium. In addition, we estimated the energy of the unstable ion He^{--}:

$$E_I = -0.198 + 0.038\, i \text{ (a. u.)}$$