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Variational principle for critical parameters of quantum systems

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Abstract. The variational principle for eigenvalue problems with a nonidentity weight operator is used to establish upper or lower bounds on critical parameters of quantum systems. Three problems from atomic physics are considered as examples. Critical screening parameters for the exponentially screened Coulomb potential are found using a trial function with one nonlinear variational parameter. The critical charge for the helium isoelectronic series is found using a Hylleraas-type trial function. Finally, critical charges for the same system subjected to a magnetic field are found using a product of two hydrogen-like basis sets.

1. Introduction

The variational principle for eigenvalue problems is a well known method and has been widely used in quantum calculations since the foundation of quantum mechanics. For the eigenvalue equation of the form

$$L(\psi) = \lambda M(\psi) \tag{1}$$

where L and M are self-adjoint semi-bounded operators, the variational principle reads (Morse and Feshbach 1953):

$$\delta[\lambda] = \delta\left[\int \psi L(\psi)\,\mathrm{d}V \Big/ \int \psi M(\psi)\,\mathrm{d}V\right] = 0. \tag{2}$$

For a time-independent Schrödinger equation, M and λ are usually considered as the identity operator and the energy, in this case equation (2) represents the variational principle for the energy. Here, we point out the usefulness of the variational principle with a non-identity 'weight' operator, M, for calculations of critical parameters of quantum mechanical systems.

We consider a Hamiltonian $H(\gamma)$ that depends on some continuous parameter. We call the parameter $\gamma = \gamma_c$ *critical* if the energy eigenvalue passes the border of the continuum spectrum $E_I(\gamma)$. For example, the border of the continuum spectrum is zero energy for one particle in a finite-range potential, and it is the energy of the positive ion for an atom. If the Hamiltonian and the border of the continuum depend linearly on the parameter γ, i.e. $H(\gamma) = H_0 + H_1\gamma$, $E_I(\gamma) = E_0 + E_1\gamma$, then the Schrödinger equation for the critical parameter,

$$H(\gamma_c)\psi = E_I(\gamma_c)\psi \tag{3}$$

takes the form of equation (1) where $L = H_0 - E_0$, $M = E_1 - H_1$, and $\lambda = \gamma_c$, in which case the variational principle can be used immediately. Often, a linear dependence on γ can be achieved by an appropriate scaling transformation before using the variational principle.

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A similar approach was used previously for critical screening parameters of the exponentially screened (Hulthén and Laurikainen 1951) and of the cut-off (Dutt *et al* 1985) Coulomb potentials. Here we present a further demonstration of the power of the general variational principle, equation (2), to obtain very accurate critical parameters for both simple one-degree-of-freedom problems such as the Yukawa potential and for problems of several degrees of freedom such as two-electron atoms in a magnetic field. To the best of our knowledge, this general variational principle is used here for the first time to calculate critical parameters for several degrees of freedom. Let us consider several examples to illustrate this approach.

2. Yukawa potential

Thoughout the present paper we use atomic units $\overline{h} = e = m = 1$. The radial Schrödinger equation for one particle in a Yukawa potential, $v(r) = -\exp(-\delta r)/r$, after the scaling transformation $r \to r/\delta$, takes the form

$$\left[-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2} - \delta^{-1}\frac{\exp(-r)}{r} - \delta^{-2}E\right]P(r) = 0 \tag{4}$$

where l is the azimuthal quantum number, δ the screening parameter, E the energy, and $P(r)$ the radial wavefunction multiplied by r. For a sufficiently large critical screening parameter $\delta = \delta_c$ the energy reaches the ionization border $E_I = 0$.

Since both $\delta^{-2}E$ and δ^{-1} enter equation (4) linearly, each of these quantities can be determined by the variational method if another one is known in advance. Minimizing the energy is a common use of the variational method in which case L is equal to the Hamiltonian and $M = 1$. Since for calculating critical parameters the energy is known in advance ($E = 0$) and δ is a variable to be found, here we minimize the quantity $\lambda = \delta_c^{-1}$ by choosing $L = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + \frac{l(l+1)}{2r^2}$ and $M = \exp(-r)/r$, i.e. the Yukawa part of the Hamiltonian (4) is shifted to the rhs.

We are looking for an extremum of the functional

$$W = \int \psi L(\psi)\,\mathrm{d}r \Big/ \int \psi M(\psi)\,\mathrm{d}r \tag{5}$$

using a trial function with only one variational parameter α:

$$\tilde{P}(r) = r^{-l}\left(1 - \mathrm{e}^{-\alpha r}\sum_{n=0}^{2l}\frac{\alpha^n}{n!}r^n\right). \tag{6}$$

The function, equation (6), behaves like $\tilde{P}(r) \sim r^{l+1}$ at $r \to 0$ and $\tilde{P}(r) \sim r^{-l}$ at $r \to \infty$ which is consistent with the behaviour of the general solution of the radial Schrödinger equation at zero energy.

The functional, equation (5), appears to have a minimum at a certain $\alpha = \alpha_{\min}$, these values are listed in table 1 for different values of l. Its minimum gives an approximation for the eigenvalue $\tilde{\lambda}$. The corresponding approximations for the critical screening parameter $\tilde{\delta}_c = \tilde{\lambda}^{-1}$ together with the exact critical screening parameters, which have been found numerically by integration of the Schrödinger equation, are listed in the last two columns of table 1. The variational method yields excellent lower bounds for the critical screening parameters of the lowest states in each subspace l.

Hulthén and Laurikainen (1951) used the variational method for the equivalent equation $(\mathrm{d}^2\phi/\mathrm{d}x^2)+[a+b(\mathrm{e}^{-x}/x)]\phi = 0$ with a treated as the known parameter and b as the eigenvalue. Since their zero-energy trial function $(1 - \mathrm{e}^{-x})\sum_{\nu=0}^{n} h_\nu \mathrm{e}^{-\nu x}$ is more elaborate than our trial

Table 1. Results of minimization of the functional, equation (5), for the Yukawa potential with a one-parameter trial function, equation (6). The exact critical parameters are given in the last column for comparison.

l	$\alpha_{\min}$	$\tilde{\delta}_c$	δ_c
0	1.535	1.190 213	1.190 612
		1.190 524[a]	
		1.190 580[a]	
		1.190 604[a]	
1	2.534	0.219 800	0.220 217
2	3.525	0.091 085	0.091 345
3	4.517	0.049 670	0.049 831
4	5.513	0.031 240	0.031 344
5	6.510	0.021 455	0.021 525
6	7.507	0.015 642	0.015 691
7	8.506	0.011 909	0.011 945

[a] Variational results of Hulthén and Laurikainen (1951) for the trial function with one, two and three effective parameters ($n = 1$, 2 and 3).

function $1-\mathrm{e}^{-\alpha x}$ (equation (6) at $l = 0$), their variational results (displayed in terms of $\delta = 2/b$ in table 1) are more accurate.

3. Two-electron atoms

The minimum nuclear charge Z for which the given state of an atom remains a bound state is called the critical charge Z_c.

The calculation of Z_c for two-electron atoms has a long history (Brändas and Goscinski 1972, Stillinger 1966, Stillinger and Stillinger 1974, Stillinger and Weber 1974, Reinhardt 1977) with controversial results of whether or not the value of Z_c^{-1} is the same as the radius of convergence of the perturbation series in $1/Z$, Z_*^{-1}. Baker *et al* (1990) have performed a 400-order perturbation calculation to resolve this controversy and found that $Z_* = Z_c$ where numerically $Z_*^{-1} \approx 1.097\,66$. Using the Euler transformation of the series to accelerate its convergence, Ivanov (1995) estimated the value of the radius of convergence as $Z_*^{-1} \approx 1.097\,660\,79$.

The Schrödinger equation for a two-electron atom, after the scaling transformation $r \to r/Z$, takes the form

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + Z^{-1}\frac{1}{r_{12}} - Z^{-2}E\right]\psi = 0 \tag{7}$$

where Z is the charge of the nucleus and E is the energy (in atomic units). For a sufficiently small nuclear charge, at $Z = Z_c$ the energy reaches the ionization border $E_I = -Z^2/2$, which is the energy of a one-electron atom. The equation for Z_c has the form of a general eigenvalue equation (1) in which $L = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - 1/r_1 - 1/r_2 + \frac{1}{2}$, $M = 1/r_{12}$, and $\lambda = -Z_c^{-1}$. We are looking for an extremum of the functional, equation (5), using a Hylleraas-type trial function of the form

$$\psi_N = \sum_{i+j^2+k^2 \leqslant N} C_{i,j,k}[r_1^i r_2^j \exp(-ar_1 - br_2) + r_2^i r_1^j \exp(-ar_2 - br_1)]\exp(-cr_{12})r_{12}^k. \tag{8}$$

The restriction on the summation indices $i + j^2 + k^2 \leqslant N$ is used instead of the more common restriction $i + j + k \leqslant N$ in order to decrease the number of terms in the sum from $\sim\frac{1}{6}N^3$ to $\sim\frac{\pi}{8}N^2$. Here, we suppose that correlation terms with higher degrees of r_{12} are relatively

Table 2. Nonlinear parameters of the Hylleraas-type trial function, equation (8).

	a	b	c
$1s^2\,{}^1S$	0.35	1.03	0.03
$2p^2\,{}^3P$	0.12	0.5	0

Table 3. The inverse of the critical charge found by minimization of the functional, equation (5), using Hylleraas-type functions, equation (8), with fixed exponents which are listed in table 2. The problem reduces to the calculation of the lowest eigenvalue of the matrix whose size increases by $\sim\frac{\pi}{8}N^2$. This matrix is computed using a multiple-precision arithmetic to avoid round-off errors. Extrapolation to $N\to\infty$ is done by Shanks transformation (Bender and Orszag 1978).

N	$1s^2\,{}^1S$	$2p^2\,{}^3P$
0	1.007 284 224	0.968 400 90
10	1.097 655 865	1.005 234 43
20	1.097 660 734	1.005 245 51
30	1.097 660 823	1.005 246 00
35	1.097 660 829	1.005 246 05
36	1.097 660 830	1.005 246 06
37	1.097 660 830	1.005 246 06
38	1.097 660 831	1.005 246 06
39	1.097 660 831	1.005 246 07
40	1.097 660 832	1.005 246 07
∞	1.097 660 833	1.005 246 08
	1.097 660 79[a]	1.004 8[b]

[a] Ivanov (1995).
[b] Brändas and Goscinski (1972).

unimportant and we suppress them by raising k to k^2. We also assume that expanding over r_2 is less important than expanding over r_1 because we are ordering the parameters a and b so that $a<b$ which means that the wavefunction $\exp(-br)$ is tighter and less influenced by the interaction term Z^{-1}/r_{12} than the wavefunction $\exp(-ar)$.

Full minimization (including nonlinear parameters a, b, and c) is done for a relatively small size of the basis set, $N\leqslant 6$. Then, we use fixed near-optimal parameters a, b, and c, which are listed in table 2, to perform minimization over linear parameters $C_{i,j,k}$ up to $N=40$. Similar computations are performed for $2p^2\,{}^3P$ state with an additional factor $(x_1y_2-y_1x_2)$ in the trial wavefunction, equation (8), (the second line in table 2) and with a different ionization energy $E_I=-Z^2/8$. Results for the critical parameter $1/Z_c=-W_{\min}$ are given in table 3. Our results are considerably more accurate than the best results obtained previously (the last line of table 3). Variational results give lower bounds for the parameter $1/Z_c$.

4. Two-electron atoms in a magnetic field

Variational calculations of energies of two-electron atoms in a constant homogeneous magnetic field were done previously using various forms of the trial wavefunction (Henry *et al* 1974, Larsen 1979, Scrinzi 1998, Becken *et al* 1999). For the present ground-state calculations of the critical charge, we use one of the simplest trial functions in the form of a linear combination of products of hydrogen-like orbitals:

$$\psi_N=\sum C_{i_1,i_2,n_1,n_2,m}[r_1^{i_1}\exp(-a_1r_1)r_2^{i_2}\exp(-a_2r_2)\cos^{n_1}(\theta_1)\cos^{n_2}(\theta_2)\sin^{|m|}(\theta_1)\sin^{|m|}(\theta_2)\times\exp(\mathrm{i}m(\varphi_1-\varphi_2))+\text{exchange}] \tag{9}$$

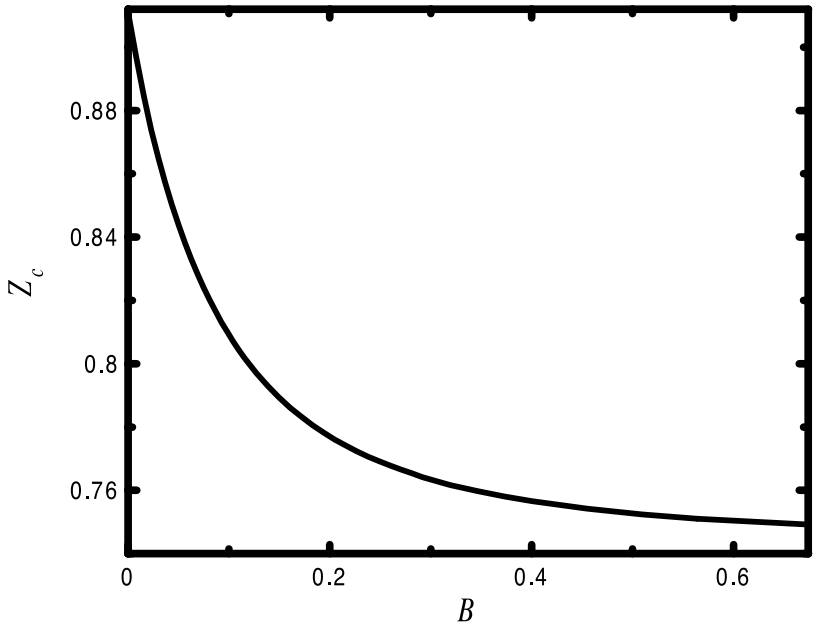

Figure 1. The dependence of the critical charge, Z_c, on the magnetic field strength B for two-electron atoms. The magnetic field is measured in atomic units (1 au $= 2.35 \times 10^9$ G).

where (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) are spherical coordinates of the electrons, and the z-axis is chosen along the direction of the field. The summation is done over indices i_1, i_2, n_1, n_2, m subject to the restrictions $i_1 + i_2^2 + m^2 \leqslant N$, $i_1 \geqslant n_1 + |m|$, $i_2 \geqslant n_2 + |m|$, where $n_1 + n_2$ is even.

In the presence of a magnetic field, the Hamiltonian in equation (7) has an additional diamagnetic interaction term $\frac{B'^2}{8}(r_1^2 \sin^2\theta_1 + r_2^2 \sin^2\theta_2)$ where $B' = B/Z^2$, and B is the magnetic field strength (in atomic units). The ionization energy is a sum of the ground-state energy of the one-electron atom in a magnetic field and the energy of a free electron in a magnetic field at the lowest Landau level, $B/2$. The energy of the one-electron atom in a magnetic field is calculated using the method of $1/D$ expansion (Germann *et al* 1995).

Minimization of the variational functional is done in a similar way to that described in section 3. For weak and medium fields, results of minimization converge with increasing N. The critical parameter is found as a function of the scaled magnetic field B'. By varying B', we determine the dependence of Z_c on $B = B'Z_c^2$ parametrically. The dependence of the critical charge on a magnetic field is shown on figure 1. The magnetic field stabilizes the atom and makes the critical charge smaller. However, for large fields this trend becomes weaker. Our results agree with an estimation $Z_c = 1/\sqrt{2} \approx 0.7$ at large B within a one-dimensional model of Brummelhuis and Ruskai (1999).

5. Conclusion

Calculation of critical parameters is of fundamental importance because it gives the boundaries of stability of a quantum system. In particular, recent calculations of critical charges for multi-electron atoms (Hogreve 1998, Sergeev and Kais 1999) have shown the nonexistence of doubly charged negative atomic ions. Our approach might be useful in combination with a recently developed finite-size scaling method for quantum systems (Neirotti *et al* 1998, Serra *et al*

1998). However, it would be desirable to develop a variational principle for critical indices that can be found by the finite-size scaling method, which are unavailable within our present approach.

In summary, we calculated critical parameters applying the generalized variational principle (2) to more complex problems than has been done previously. For several problems which are important in atomic physics, we obtained the following results: for the screened Coulomb potential, we constructed a one-parameter variational trial function which is a very accurate approximation to the threshold wavefunction for all azimuthal quantum numbers. For two-electron atoms, we calculated the critical charges for the ground and excited $2p^2\ ^3P$ states with a record accuracy and finally, we calculated, for the first time, the critical charges for two-electron atoms in the presence of a magnetic field. Although our present approach is limited to linear dependence on λ, such as for the two-electron atoms, research is underway to generalize this approach to treat larger atoms.

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