Resonant states of atoms with a variable nuclear charge

Two methods are proposed to treat resonant states of an atom with a nuclear charge less than a "critical" charge, which is a minimum charge necessary to bind N electrons. The first method represents variational approach reformulated in order to consider resonance and bound states on an equal footing. The second method represents an extrapolating scheme. It is based on one-particle model which parameters are chosen to meet known energies of a neutral atom and a negative ion. The energy of a two-electron atom was found in the entire range $0 \le Z < \infty$. In the near-threshold region $1.11 \le 1/Z \le 1.14$, our results agree with numerical calculations of the complex energy by Dubau and Ivanov. Using one-particle model, we estimated resonant energies of doubly charged negative ions for atoms with $Z \le 18$. Results for O^{--} and S^{--} are in agreement with earlier estimates.

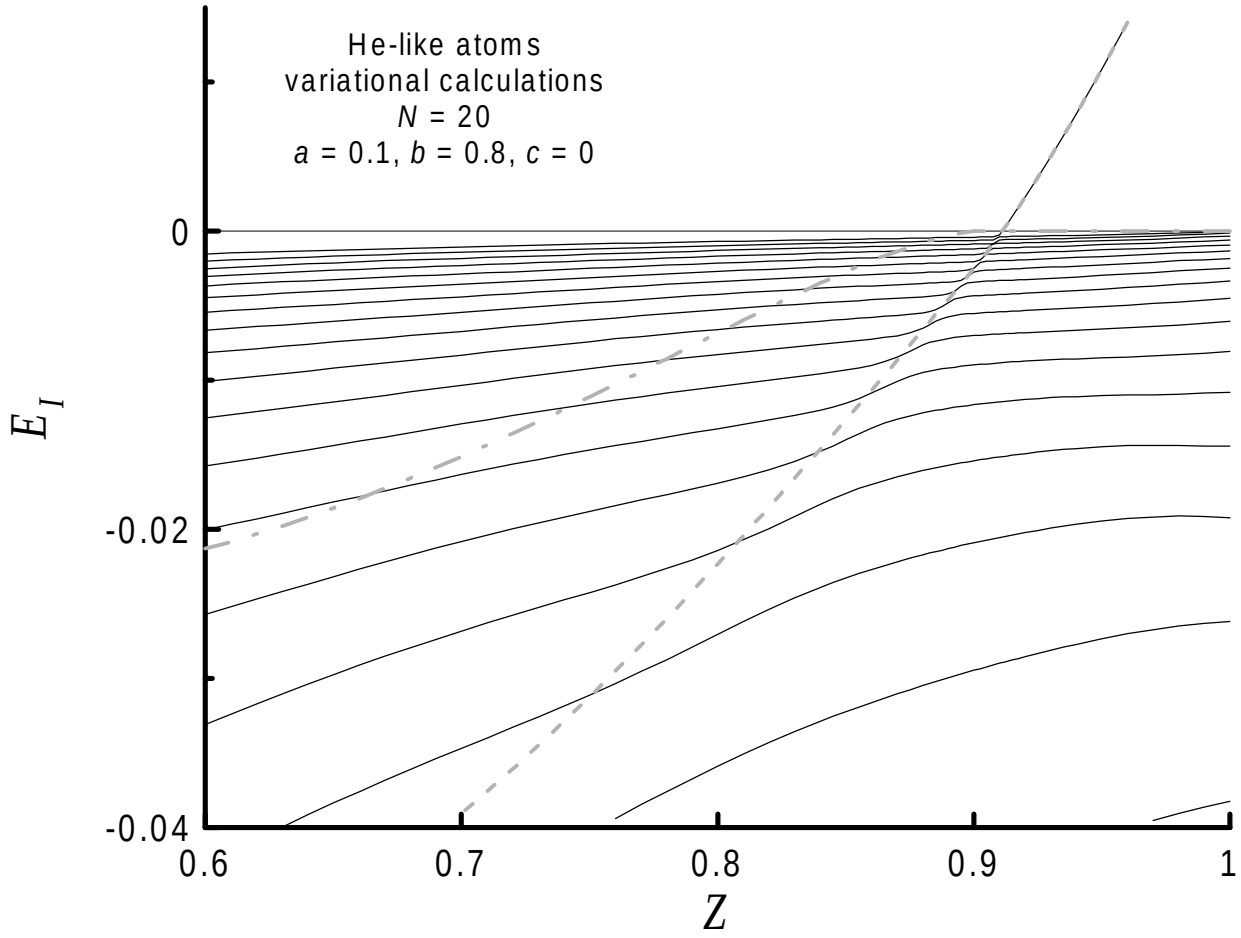
Two-electron atoms

Variational method gives accurate results for bound states of He and H^-, but it fails when the nuclear charge is less than the critical value $Z_c \approx 0.911\,028\,225$ when the state turns to a resonance. In order to understand why the variational method becomes inadequate when $Z < Z_c$, let us perform a numerical test. We use the Hylleraas trial wave function

$$\psi_N = \sum_{i+j+k \le N} C_{i,j,k} \left[r_1^i r_2^j \exp(-ar_1 - br_2) + r_2^i r_1^j \exp(-ar_2 - br_1) \right] r_{12}^k \exp(-cr_{12}) \qquad (1)$$

Minimization of the energy functional in respect to coefficients $C_{i,j,k}$ reduces to an eigenvalue problem for a finite matrix whose size increases $\sim N^3/6$. We found several lowest eigenvalues for $N = 20$, $a = 0.1$, $b = 0.8$, and $c = 0$.

The ionization energy $E_1 = -E - Z^2/2$ as a function of the nuclear charge is shown on the following figure (solid lines).



If $Z > Z_c$ then the lowest level (corresponding to maximum ionization energy, the upper curve on the figure) gives the bound state energy (positive ionization energy). The figure shows that the upper curve rapidly bends to zero after going below Z_c. It means that the variational method gives a trivial result $E_I = 0$ when the bound state ceases to exist. However, all the curves (corresponding both to the minimum and to higher eigenvalues) also shown at the figure exhibit a typical avoided-crossing ladder pattern of proliferation of the bound state into continuum as a resonance. This situation is similar to the two-electron problem in finite space, compare the above figure with Fig. 3 from the paper [F. H. Stillinger, J. Chem. Phys. 45, 3623 (1966)].

In order to calculate the resonance by variational method without encountering avoided-crossings (that is the main reason why the variational method fails) we introduce a complex trial function. Up to now, we considered the exponential parameters a, b, and c as real numbers

independent on Z, and minimized the energy functional in respect to linear coefficients $C_{i,j,k}$ entering Formula (1). Alternatively, we can minimize the energy in respect to both linear and non-linear parameters (it is slightly more cumbersome numerically). In this way we found that the optimized parameters a, b, and c are real for sufficiently large charges. If the charge is lower than some value (see the table below), then the minimum of the energy functional no more exists (note that the situation is different from minimizing over the linear parameters only when the minimum of the energy functional *always* exists because a real symmetric matrix always has a minimum real eigenvalue). An analytic continuation of a minimum of some function when this minimum ceases to exist represents a complex stationary point. We found the parameters a, b, and c as complex stationary points numerically in the range $0 \le Z \le 1$ up to $N = 5$ (for larger N, the computational time is too long). The result for $N = 5$ is shown at the above figure. The real part is a dashed line, and the imaginary part of the ionization energy is a dot-dashed line. By allowing parameters of the trial function to be complex-valued, we eliminated avoided-crossings and made the results to converge with increase of N. It is interesting that the traditional variational method (with real parameters a, b, and c) gives very accurate results at inflection points, between adjacent avoided-crossings (see the figure), but it never reproduces the imaginary part (the width) of the resonance.

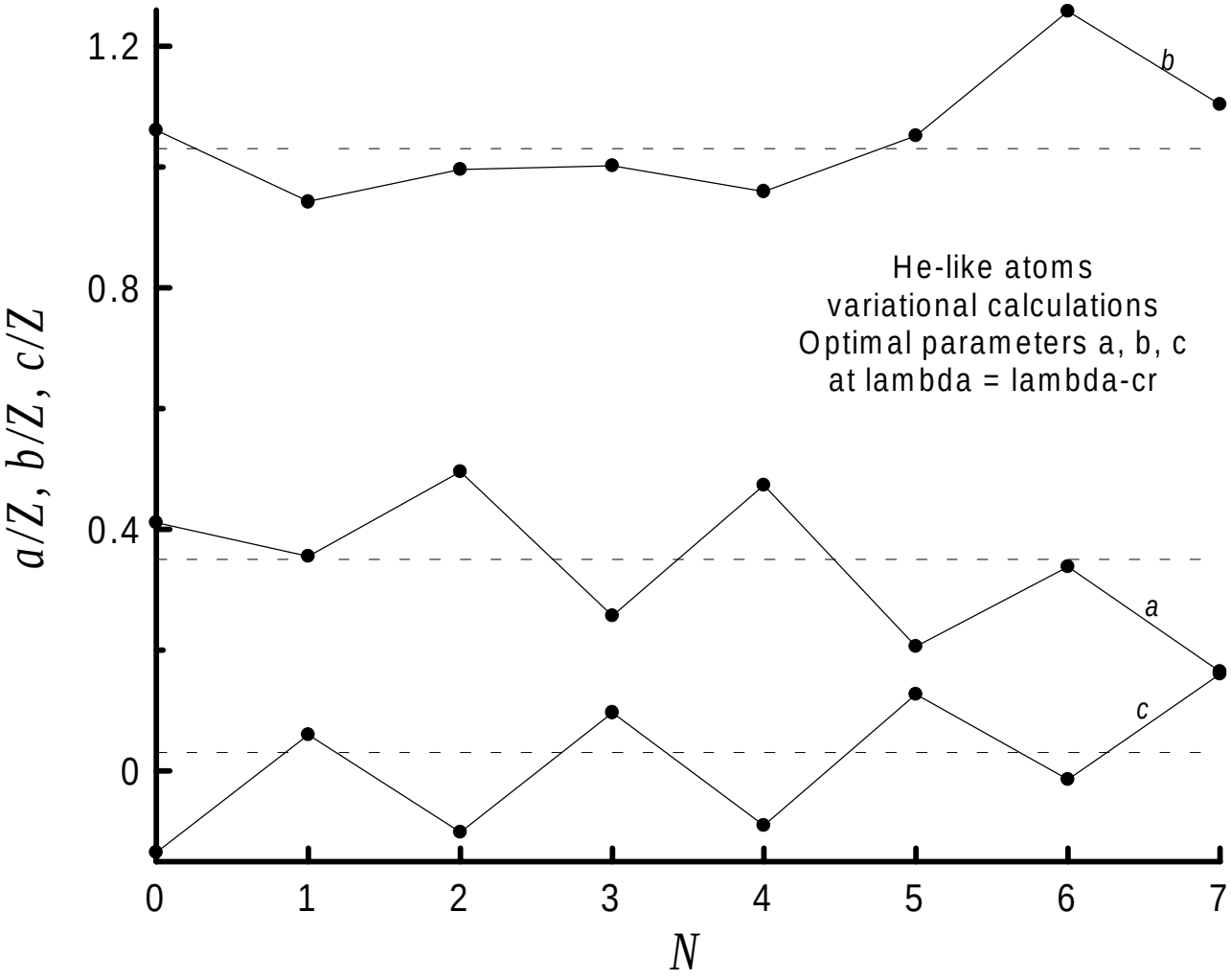
Let us consider the variational results from the point of view of analytic structure of the energy as a function of the nuclear charge. If the exponential parameters a, b, and c are real, then the energy (shown by solid lines at the figure) is real and does not have singularities at the real axis. However, for sufficiently small charge there is a pair of complex conjugate square root branch points close to the real axis joining each branch of the energy function (shown as a continuous solid curve at the above figure) with the neighbor branch (the nearest curve that lies above or below). In contrast, if the exponential parameters a, b, and c are allowed to accept complex values then the variational energy (shown by dashed and dot-dashed curves) has a single singularity at the real axis at the point where the minimum of the energy functional disappears and turns to a complex stationary point. This singularity models a singularity of the exact energy at the "critical" charge where the system goes from a bound state to a quasistationary state. Positions of this singularity $Z_*^{(N)}$ for different N (responsible for a size of the basis set) are listed at the following table.

N	$Z_*^{(N)}$	$Z_c^{(N)}$
0	0.883 998	0.925 879
1	0.868 302	0.915 729
2	0.889 957	0.913 198
3	0.891 584	0.911 369
4		0.911 265
5	0.899 586	0.911 081
6		0.911 070
[St., 1966]	0.894 1	0.911 2
[Baker et al]	0.911 028	

The numerical evidence is that the variational singularities $Z_*^{(N)}$ give lower bound for the critical charge $Z_c \approx 0.911028...$ and converge with increase of N although the convergence is not monotonous. The table lists also variational "critical" charges $Z_c^{(N)}$ defined as zeroes of the ionization energy $-E^{(N)}(Z)-Z^2/2$. The "critical" charges $Z_c^{(N)}$ could be calculated by solving a generalized eigenvalue problem by a variational method [J. Phys. A], they always give upper bounds for Z_c. We found that convergence of $Z_c^{(N)}$ to the critical charge is much faster than that of $Z_*^{(N)}$. By extending variational calculations of $Z_c^{(N)}$ to higher N, the most accurate estimation of the critical charge was found earlier [J. Phys. A]. Calculations of $Z_*^{(N)}$ are generally more difficult than that of $Z_c^{(N)}$ because they represent a singularity. They converge to the singularity Z_* of the function $E(Z)$, which is believed to limit the radius of convergence of the $1/Z$ expansion to $1/Z_*$ […]. According to an earlier hypothesis based on analysis of the $1/Z$ perturbation series [F. H. Stillinger, J. Chem. Phys. 45, 3623 (1966)], Z_* is slightly smaller than Z_c (see the above table) which means that $E(Z_*)$ lies above the continuum, but still corresponds to a localized wavefunction. More elaborate computations of the $1/Z$ series and its analysis by Baker et al. […] show that Z_* and Z_c are equal.

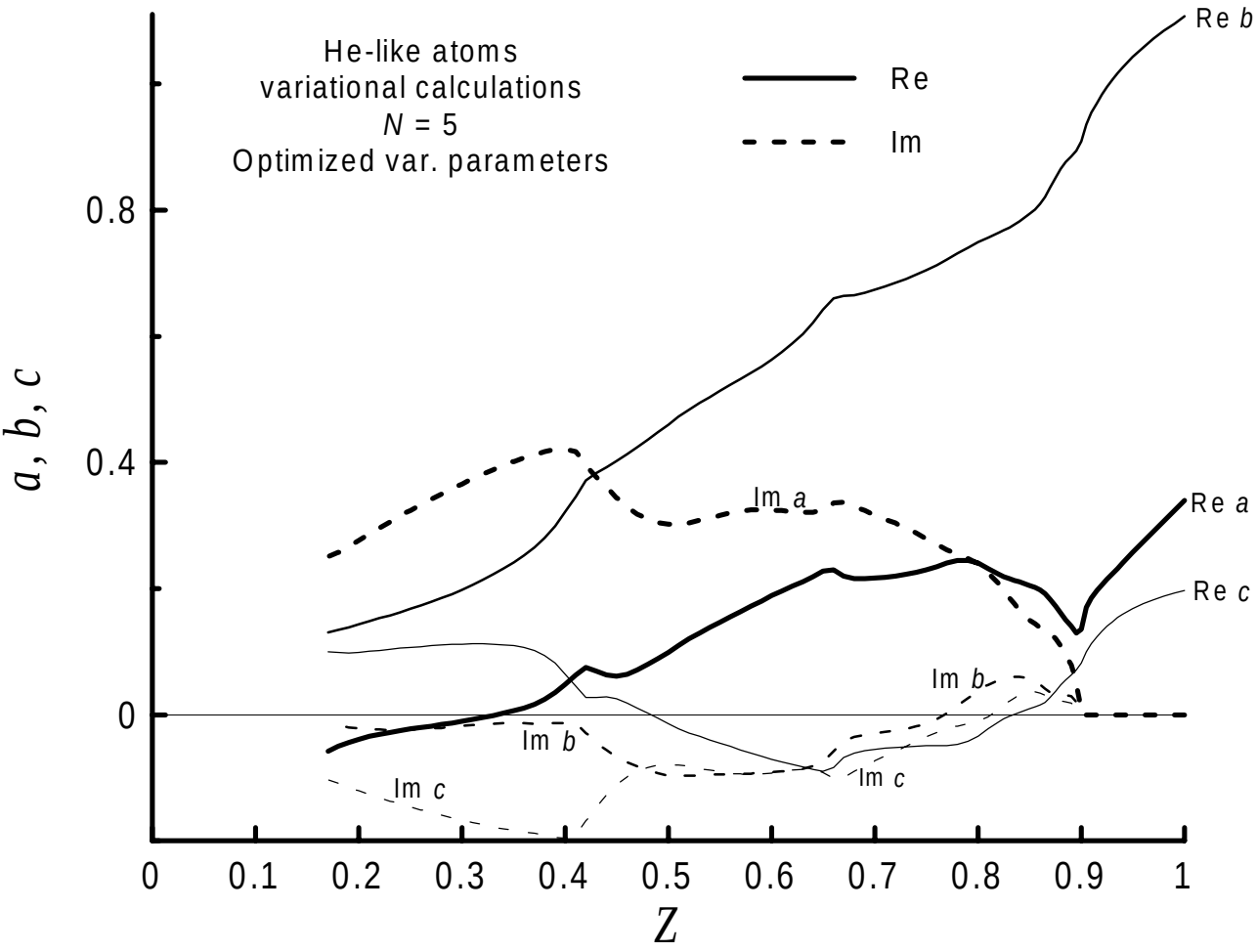
We used the complex parameters a, b, and c calculated for particular $N=5$ to extend calculations to higher N by optimizing the linear coefficients $C_{i,j,k}$ only. We found that "almost exact" variational energy calculated at $N=12$ differs from the variational energy at $N=5$ shown at Figure 1 in the amount of less than $0.5\cdot10^{-4}$.

Calculations show that behavior of the parameters a, b, and c which are a stationary point of the energy functional is more unpredictable than that of the energy. Dependence of a, b, and c on N at $Z = Z_c$ is shown at the following figure.



It seems that the parameters erratically oscillate as N increases. In our previous paper [J. Phys. A], we used near-average parameters $a/Z = 0.35$, $b/Z = 1.03$, and $c/Z = 0.03$ shown by dashed lines on the figure to perform large-N calculations of Z_c (by minimizing the linear parameters only).

Dependence of a, b and c on Z for $N = 5$ is shown on the following figure.



The parameters are continuous function of Z with a square root singularity at $Z = Z_*$, below which they become complex-valued. Numerical results show many erratic swerves on the curves, this fact probably indicates existence of many singularities close to the real axis.

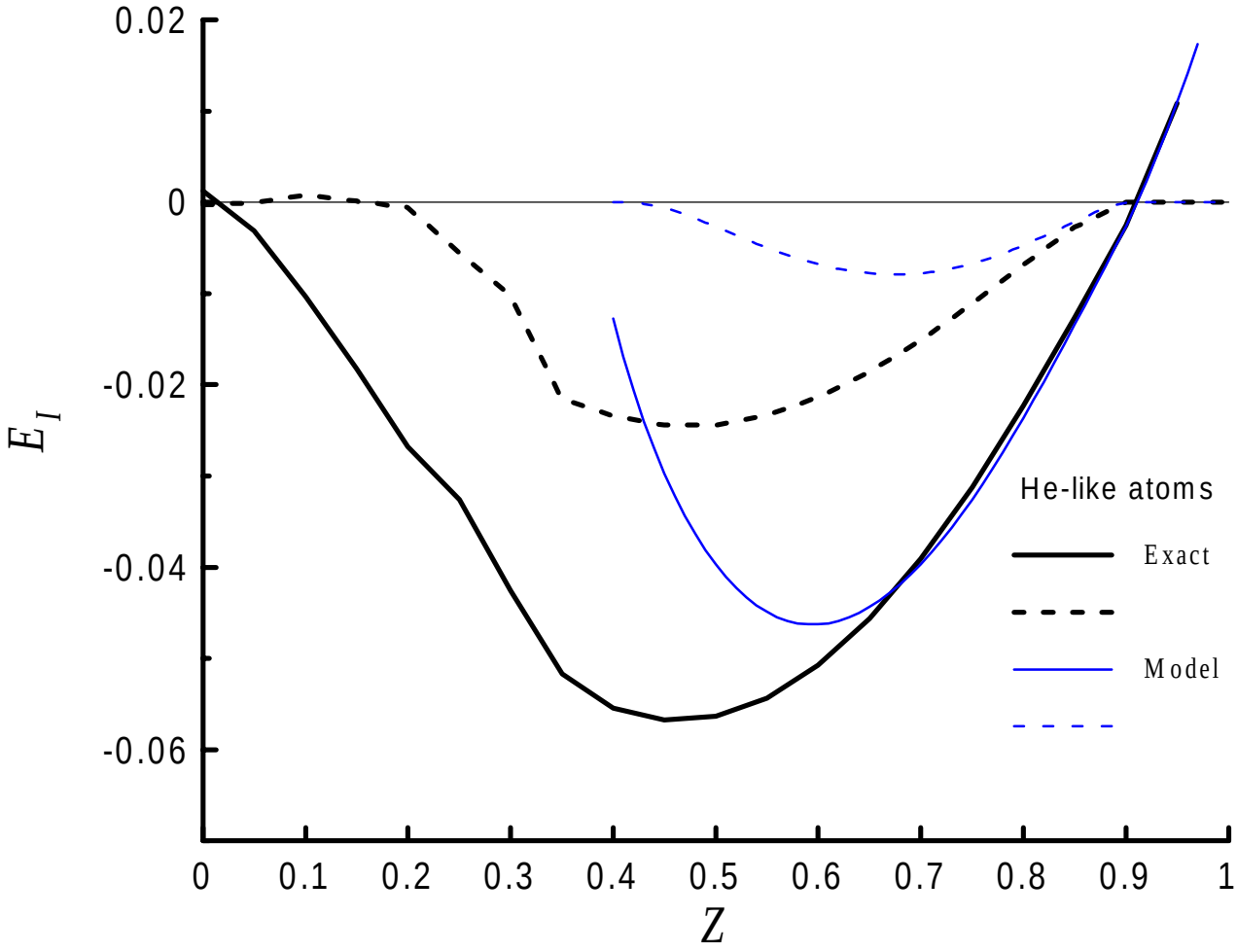
Most of the above features are typical for any system passing from a bound to a quasistationary state that is treated variationally, for example for Ne isoelectronic series with a nuclear charge below $Z_* \approx 8.74$ [D. R. Herrick, F. H. Stillinger, J. Chem. Phys. 62, 4360, 1975].

The above method is a more general version of the complex rotation or the complex stabilization method [Y. K. Ho. Phys. Reports, 99, 1 (1983)]. Instead of one complex variational parameter (rotation angle), we are using three complex variational parameters a, b, and c (standing in exponents of the trial function).

Dubau and Ivanov [J. Phys. B 31, 3335 (1998)] calculated the two-electron atom resonance in the vicinity of the critical charge using $1/Z$ expansion and the complex rotation method. Their results agree with our calculation, see the following table.

$1/Z$	$-Z^{-2}\,\mathrm{Re}E$	$-Z^{-2}\,\mathrm{Im}E$	$-Z^{-2}\,\mathrm{Im}E$ (CRM […])	$-Z^{-2}\,\mathrm{Im}E$ (model)
1.11	0.497 131	0.000 050	0.000 06	~0.000 03
1.12	0.494 953	0.000 286	0.000 28	0.000 24
1.13	0.492 792	0.000 686	0.000 70	0.000 57
1.14	0.490 616	0.001 207	0.001 21	0.000 98

We extended calculations of the resonance to the range of $0 \le Z \le 1$. Results are shown at the following figure.



A real part of the ionization energy is always negative at $0<Z<Z_c$. It reaches its minimum at $Z\approx 0.45$, and the width reaches its maximum approximately at the same point. When $Z\to 0$, both real and imaginary parts tend to zero.

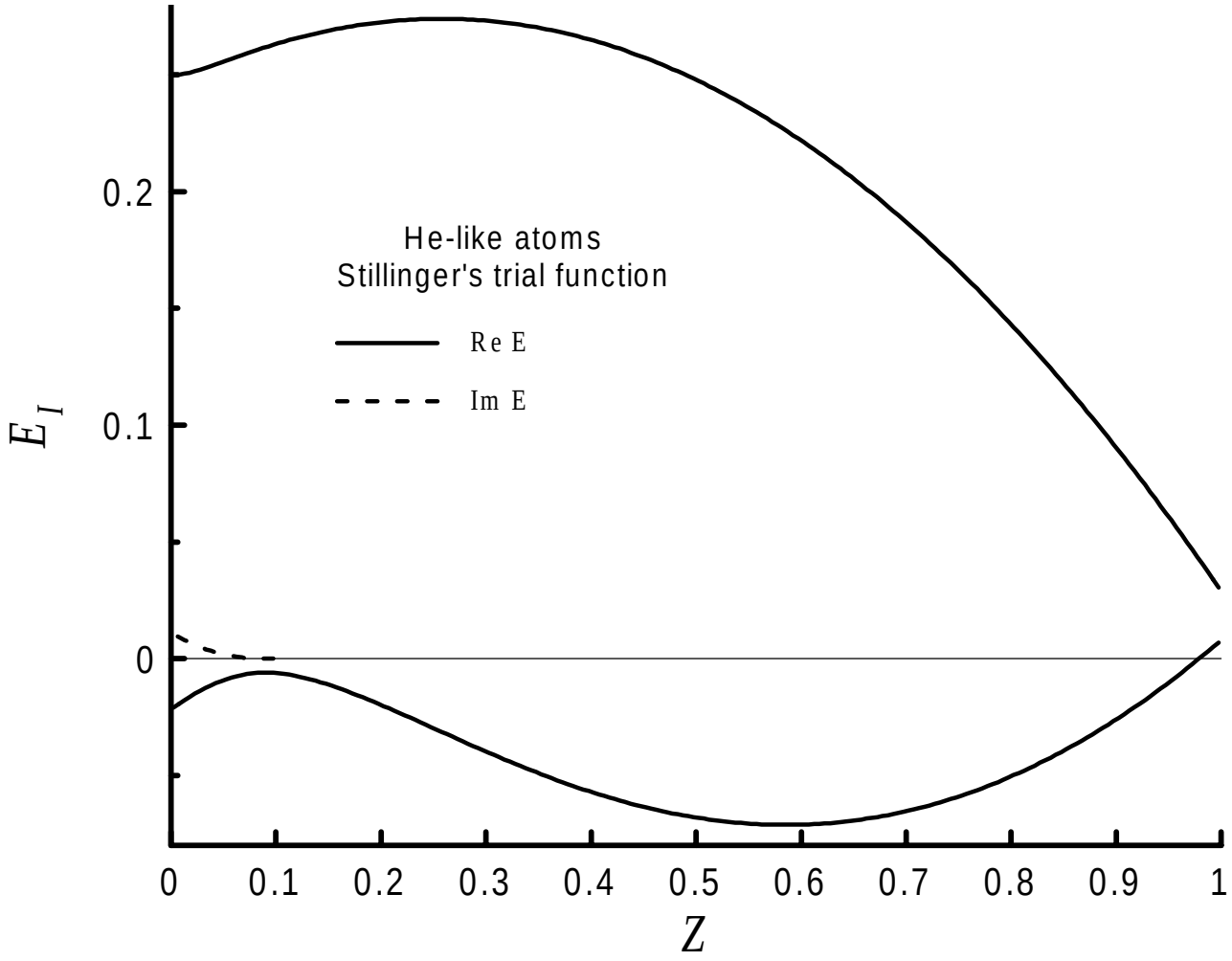
Our results for small Z apparently contradict to a tentative supposition of [Stillinger 1966] that

$$E(Z)=-1/4-4Z^2+256Z^4+O(Z^5) \qquad (2)$$

as $Z\to 0$ at any ray in a complex plane. Stillinger found that a small negative charge corresponds after suitable scaling to a tightly bound "di-electron" moving in a Coulomb field of the nucleus and he derived the behavior of $E(Z)$ as $Z\to -0$. He considered also the simplest trial function

$$\phi_{\rm var}(\mathbf{r}_1,\mathbf{r}_2)=\exp[-\alpha(r_1+r_2)-\beta r_{12}] \tag{3}$$

and he found that $E_{\rm var}(Z)=-1/4-4Z^2+448Z^4+...$ at $Z\to 0$ in a good agreement with (2). We re-examined variational calculations with the trial function (3) and revealed that Stillinger actually dealt with two different branches of the variational energy which are displayed at the figure below.



The first branch (lower curve at the figure) corresponds to a physical wavefunction with a positive exponential parameter α at sufficiently large Z. It goes almost to zero as the charge decreases (it becomes complex below $Z_*=0.0846$). The second branch corresponds to a divergent wavefunction with a negative α. It goes to –1/4 as the charge decreases and then turns to a physical branch with $\alpha>1$ at negative Z. The second branch is also present in our calculations with the trial function (1),

but we always disregard it. According to our numerical results, the energy goes to zero at $Z \to 0$ (see the figure 2).

However, our results seem to confirm the hypothesis of existence of one more singular point somewhere in the interval (0.1,0.2) below which the energy becomes real. This hypothesis was derived by [Stillinger 1966] from his supposition (2) and later confirmed by [Dubau and Ivanov 1998].

The figure 2 shows also results of using an approximate one-particle model that will be introduced below and that will be applied for many-electron atoms.

Many-electron atoms

Applying the complex rotation method to systems of more than three charged particles faces slow convergence because of difficulty to simulate the oscillatory character of the wave functions [Y. K. Ho, Phys. Reports, 99, 1, 1983].

The present study deals with the ground state ionization energy of a multi-electron atom considered as a function of a nuclear charge. Since a size of the variational basis set grows exponentially with increase of a number of electrons, we choose here to follow a simpler path. We use the reliable data for the ionization energy of a negative ion, a neutral atom and the isoelectronic positive ions, which were calculated or experimentally measured. We are going to use here some sort of extrapolating technique in order to find a complex energy of a doubly charged negative ion. In contrast to simple extrapolating such as polynomial fits or analytic formulas with a few fitting parameters [B. Eldén, J. Chem. Phys. 33, 98 (1960)], we are solving here a one-particle Schrödinger equation with a potential that models a movement of a loosely bound valent electron that is going to dissociate when the charge approaches its critical value. We believe that this model is realistic in a vicinity of the critical charge and effectively reproduces the non-trivial singularity [Ivanov 1995] of the ionization energy at the critical charge. Herric and Stillinger [1975] used for Ne isoelectronic series a polynomial fitting formula plus a singular term $\sim (Z - Z_*)^{3/2}$. Their method correctly

reproduces a similar singularity of a variational energy $\sim (Z - Z_*^{(N)})^{3/2}$, but it fails for the exact energy, which has a less trivial singularity as it was established by Ivanov and Dubau [1998] (at least for two-electron atoms).

Description of the one-particle model

For a given atom with N electrons and a nuclear charge Z, let us consider a spherically-symmetric potential (also known as Hellmann potential [B. Hellmann, J. Chem. Phys. 3, 61 (1935)])

$$V(r) = -\frac{1}{r} + \frac{\gamma}{r}\left(1 - e^{-\delta r}\right) \tag{4}$$

with $\gamma = (N-1)/Z$.

Since in the neighborhood of the critical charge, particularly for the negative hydrogen ion [Rau 1996], one of the electrons is held much farther from the nucleus than the others, we suggest a one-particle model of this electron in an effective potential of the atomic core comprising of the nucleus and $N-1$ electrons. In the scaled coordinates $r \to Zr$, this potential is approximated by our model potential (4). Our approximation is asymptotically correct both at small and at large distances from the nucleus where the scaled atomic core potential tends to $-1/r$ and to $-(Z-N+1)/(Zr)$ respectively. The transition between the two different asymptotic regimes occurs at distances roughly equal to $1/\delta$ that is about the atomic core radius.

The second parameter of the model potential (4), δ, is chosen so that the ionization energy in the potential (4) is equal to the scaled ionization energy $Z^{-2}E_{\mathrm{I}}(Z)$ of the atom. Note that for atoms with more than two electrons, we consider here an excited state in the potential (4) with the same spherical quantum numbers (n,l) as quantum numbers of the loosely bound electron on an external atomic shell (in this aspect our approach differs from the method of pseudo-potentials [Callaway 1958] that deals with the ground state in a potential with an additional repulsive term necessary take into account orthogonality conditions). In this way, we map an arbitrary atom, which is characterized by a pair of numbers (N,Z) to the model one-particle system (4), which is characterized by a pair of parameters (γ,δ). Results of fitting the parameter δ for elements with $N \le 10$ in our previous study

[Int. J. Q. Ch.] give evidence that δ depends on $1/Z$ almost linearly. In summary, our model (4) effectively eliminates the singularity in the energy function $E_{\mathrm{I}}(Z)$ to be extrapolated by replacing it with a weakly varying function $\delta(Z)$ that can be accurately extrapolated by a linear dependence on $1/Z$ without taking into account a complex singularity at $Z = Z_*$. In our previous study [Int. J. Q. Ch.], we fitted the parameter δ to meet the known binding energy of the neutral atom and its isoelectronic negative ion and then found δ as a function of $1/Z$ by a linear extrapolation. After that, we solved Schrödinger equation with the potential (4) and found some kind of extrapolation of the ionization energy of an atom to the range of $Z < N - 1$. Finally, by localizing a zero of the ionization energy, we found critical charges for most of atoms with $N \le 86$. In the present paper, we use the same technique to find resonances of doubly charged negative ions by calculating the ionization energy at $Z = N - 2$.

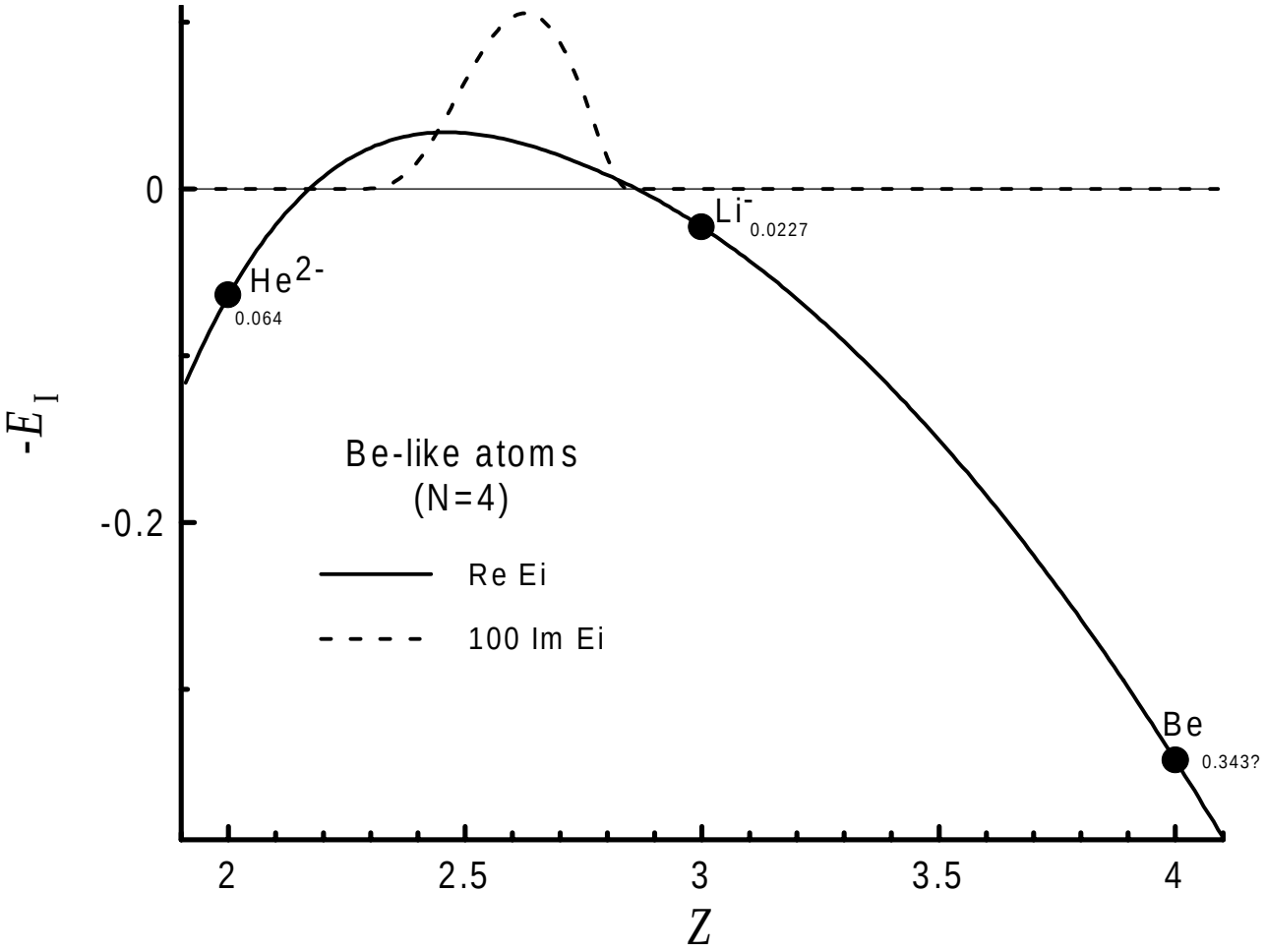
Results

For two-electron isoelectronic series, the parameter δ is 1.066 and 0.881 for He and H^- respectively. Decreasing of δ for H^- means increasing of the core radius that is induced by stronger repulsion between electrons. Results of extrapolating the ionization energy to the range $Z < 1$ with δ assumed as a linear function of $1/Z$ are shown on Fig. 3 together with more accurate variational results. As it was expected, the one-particle model gives fairly accurate results in the vicinity of the critical charge where it models the threshold singularity. Here, the real part is approximated more accurately than the imaginary part because the singularity manifests mostly in the imaginary part. Numerical results for the imaginary part are given in Table 2. Since in the latter case the charge is close to the critical charge, we slightly corrected location of the singularity in our model by fitting δ at points $Z = Z_{\mathrm{c}} \approx 0.911$ and $Z = 2$ instead of fitting it at points $Z = 1$ and $Z = 2$.

For three-electron isoelectronic series, our model cannot be used in the same way because He^- does not exist and we don't know the behavior near the singular point $Z_{\mathrm{c}} = 2$. It is reasonable to expect that the resonance H^{--} is highly unstable because the isoelectronic ion He^- (with larger charge of the nucleus) is already unstable. We tried to extrapolate the ionization energy by fitting δ at points

$Z = 4$ (Be^+) and $Z = 3$ with subsequent extrapolation of δ to $Z = 1$ by a linear function in $1/Z$ and found a broad resonance with $E_I = -0.109 - 0.089i$ for H^{--}.

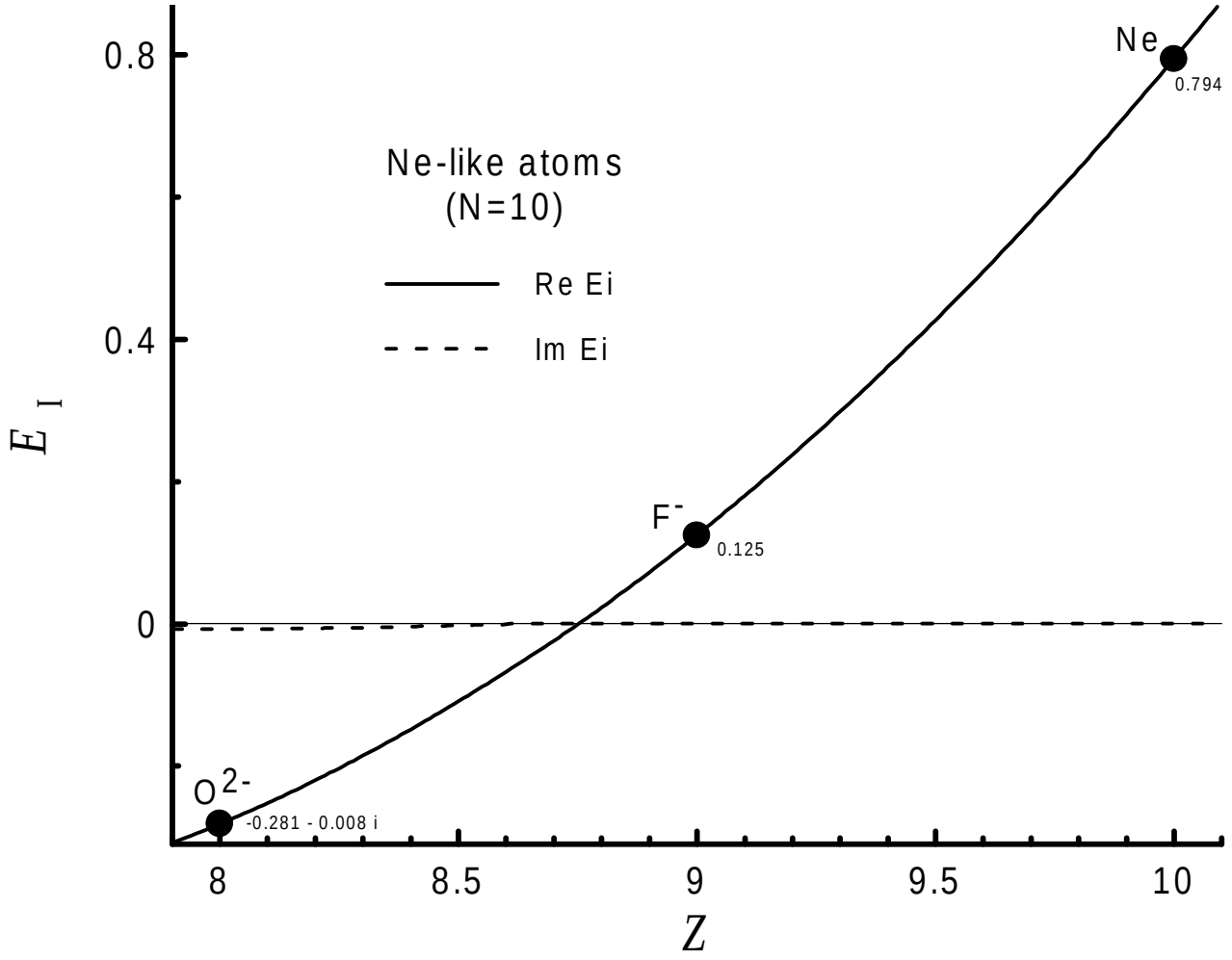
For four-electron isoelectronic series, results of using our model for extrapolating the ionization energy are shown on the following figure.



We found that the curve hits the border of continuum spectrum $E_I = 0$ at $Z_c = 2.864$ [Int. J. Q. Ch.] and again at $Z'_c = 2.17$. Very small imaginary part exists in the interval $Z'_c < Z < Z_c$. The extrapolation gives *positive* ionization energy for He^{--}, $E_I = 0.064$. Since a bound state of He^{--} does not exist, it means that we deal with a virtual state with an exponentially growing wave function. It may be also possible, that because of its limitations our method fails for He^{--} ion. We found positive

ionization energies for another doubly charged negative ions of noble gases, for example Ne^{--} (see the table below).

The doubly charged negative ion of oxygen in the same electronic configuration as a closed-shell 10-electron configuration of a neutral atom of neon is the system that was studied theoretically using various methods, see the table below (however, this relatively stable ion was never observed experimentally). The extrapolated ionization energy as a function of Z is shown on the following figure.



Comparison of the ionization energy of O^{--} found by different methods is given in the following table.

Reference	**Method**	$-E_I$, eV
Clementi 1964	Hartree-Fock	8.30
Huzinaga 1973	Hartree-Fock-Roothaan*	7.68
Cantor 1973	Combining thermochemical data	7.94
Herrick 1975	Extrapolating formula including 3/2 power term	$5.38 - 0.65\,i$
	Eldén's three-parameter formula	5.31
	Kaufman's two-parameter formula	7.17
	Kaufman's three-parameter formula	6.53
	Quadratic fit	7.09
Gadzuk 1989	Extrapolating of isoelectronic cases	8.8
Robicheaux 1994	Polynomial fit	7.2 ($\Gamma > 1$)
Present paper	One-particle model	$7.65 - 0.22\,i$

* Huzinaga listed the total energy. We found the ionization energy by subtracting Hartree-Fock total energy of the corresponding singly charged negative ion that is listed in papers of Clementi (1963, 1963a).

For critical discussion of some of these results, see the paper of Herrick (1975). Our result for resonance position is in agreement with most of the above results. However, our prediction of the resonance width is significantly lower than that of Herrick. It may be attributed to the fact that Herrick's 3/2-power term (responsible for the width) is far from the actual singular behavior or to the fact that our model systematically underestimates the width as it happens for two-electron atoms.

We extended calculations of resonances of doubly charged negative ions to the first two rows of the periodic table (here, we considered only that ions for which an isoelectronic singly charged negative ion is stable, for example we omitted C^{--} because N^- does not exist). Results are listed in the table below.

Z	$-E_I$, eV
2 He^{--}	–1.73
4 Be^{--}	3.43 – 0.03 i
5 B^{--}	4.88 – 0.10 i
6 C^{--}	6.11[b]
7 N^{--}	7.48 – 0.26 i 7.97[a] 7.07[b]
10 Ne^{--}	–0.92
12 Mg^{--}	1.79
13 Al^{--}	3.44 – 0.01 i
14 Si^{--}	4.76 – 0.06 i 4.12[b]
15 P^{--}	4.95 – 0.06 i 4.47[b]
16 S^{--}	4.91 – 0.05 i 4.62[b] 4.7[c]

[a] Hartree-Fock results of Clementi (1964)

[b] Hartree-Fock-Roothaan results of Huzinaga (1973)

[c] Polynomial fit of Robicheaux (1994)

For the closed shell ion S^{--}, our ionization energy is slightly smaller than the previous estimates. The width for S^{--} is considerably smaller than for the ion O^{--} in agreement with an argument of Herrick and Stillinger.

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