

## Estimation of radii of convergence of Rayleigh-Schrödinger perturbation expansions: Application to the $1/Z$ expansions of two- through ten-electron atomic isoelectronic sequences

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An almost *a priori* method based on a simple theoretical model is developed for obtaining good estimates of the radius of convergence of Rayleigh-Schrödinger (RS) perturbation expansions. The procedure is applicable to the RS expansions of all stationary states of any system described by a Hamiltonian linear in a real perturbing parameter, e.g., the  $1/Z$  expansions of  $N$ -electron atomic isoelectronic sequences. The only system- and state-dependent information required is the norm of the first-order eigenfunction  $\|\psi_1\|$ . In those cases where  $\|\psi_1\|$  is inaccessible or unavailable, it is shown how adequate perturbational-variational (PV) approximations can be simply obtained. The procedure has been applied to the  $1/Z$  expansions of the ground states and several low-lying states of the  $2 \leq N \leq 10$  isoelectronic sequences. Where comparison is possible, the estimates are in close agreement with numerically obtained accurate convergence data and are greatly improved over the weak Kato-type bounds. For example, for the  $1s^2 \ ^1S$  state of the helium isoelectronic sequence, convergence is found for  $Z \geq 1$ , hence for the first time predicting convergence for  $H^-$ . Further, in harmony with physical expectations, our findings indicate that the effect of increasing  $N$  on radii of convergence is drastic; thus, for the ground states of the  $3 \leq N \leq 10$  isoelectronic sequences, the predicted region of convergence can be represented approximately by  $Z \geq 3N - 7$ . The influence of screening the nucleus in compensating for the effect of increasing  $N$  is investigated and it is shown how the radius of convergence can be maximized by optimal screening. A PV method is introduced for obtaining estimates of the optimal screening parameter for arbitrary  $N$  and states. It is predicted that for the ground states, the optimally screened expansions will converge for  $Z \geq 3$  for the beryllium isoelectronic sequence, for  $Z \geq N$  for the boron through oxygen isoelectronic sequences, and for  $Z \geq N + 1$  for the fluorine and neon isoelectronic sequences, thus extending the application of such expansions to at least  $N = 10$ . Optimal screening is quantitatively tested for the  $1/Z$  eigenvalue expansion of the  $1s^2 2s^2 \ ^1S$  state of the beryllium isoelectronic sequence and the results are found to be in accord with predictions.

### I. INTRODUCTION

Since Rayleigh-Schrödinger (RS) perturbation theory was first introduced<sup>1</sup> in quantum mechanics, it has had a long and distinguished history as a powerful and versatile approximation method.<sup>2</sup> For a number of reasons, however, the central issue of the convergence properties of the RS perturbation expansions has been customarily ignored in most applications: Thus, the foundations of RS convergence theory, although laid<sup>3</sup> early, were not developed<sup>4,5</sup> and extended to quantum-mechanical problems<sup>4-9</sup> until fairly recently. Moreover, in practice, this general convergence theory is cumbersome to apply and has yielded disappointingly poor estimates of the radii of convergence of selected RS perturbation expansions.<sup>4(d)-9(a)</sup> Finally, the earlier applications of RS perturbation theory seldom went beyond first to, at most, second order in the eigenvalue because of the computational difficulties of evaluating the infinite summations which appear in the conventional formulation of the higher-order terms; for such low-order expansions, the question of perturbational convergence was hardly acute.

The situation, however, was radically changed by the introduction of the Hylleraas<sup>10</sup> first-order

variational principle and its subsequent generalization in the Hylleraas-Scherr-Knight<sup>11</sup> (HSK) variational-perturbational procedure which opened the door to high-order RS perturbation expansions for both ground and excited<sup>12</sup> states. As a result, in recent years there has been an enormous growth of interest<sup>11-31</sup> in the RS  $1/Z$  hydrogenic expansions<sup>10</sup> (where  $Z$  is the nuclear charge) of the non-relativistic electronic states of  $N$ -electron atomic isoelectronic sequences. Such  $1/Z$  expansions, initially obtained to low order,<sup>10,13-19</sup> have now been computed via HSK to quite high order for the ground<sup>11,20</sup> and several excited<sup>20,21</sup> states of the  $N = 2$  sequence, and by a modification<sup>22,23</sup> of HSK, to moderately high order for several states of the  $N = 2$  (Ref. 24), 3 (Ref. 25), and 4 (Ref. 26) sequences. As yet, however, the HSK procedure seems to have found little or no application to atomic isoelectronic sequences with  $N \geq 5$ . Other, more general methods for obtaining the  $1/Z$  expansions of multielectron sequences, are also available<sup>27</sup> which depend upon expressing the first-order eigenfunction of the  $N > 2$  sequence in question in terms of appropriate linear combinations of first-order eigenfunctions of the  $N = 2$  sequence. Low-order (second or third order in the eigenvalue)  $1/Z$  expansions have been obtained in this manner

for various states of the  $N=3$  [Refs. 27(c), 27(d), and 28] and 4 (Ref. 29) sequences and of the  $3 \leq N \leq 10$  sequences<sup>30</sup>; there are indications<sup>31</sup> that the extension of this procedure to higher order is feasible. The  $1/Z$  expansions of the Hartree-Fock (HF) approximation can also be calculated,<sup>32</sup> and low-order expansions have been obtained<sup>32,33,14(a),14(b),16,29,30(b),30(c)</sup> for the  $2 \leq N \leq 10$  sequences, thus enabling the correlation energy to be expressed in this form.

In view of the utility of the  $1/Z$  hydrogenic expansions and their considerable advantages<sup>34</sup> over other types of RS expansions (such as those which take the HF approximation as the zero-order eigenfunction) for atomic isoelectronic sequences, the question of their perturbational convergence has become an important issue. For example, the current pessimistic theoretical predictions<sup>8</sup> for the  $N=3$  sequence suggest divergence of the  $1/Z$  expansions for the low-lying states for all  $Z$  of interest; this has prompted a recent search<sup>35</sup> for better zero-order eigenfunctions. Further, in the HSK calculation for the  $N=4$  sequence,<sup>26</sup> it was found that the  $1/Z$  eigenvalue expansions for the states  $1s^22s^2^1S$ ,  $1s^22s2p^1P$ , and  $1s^22p^2^1S$  diverge for  $Z < 5$ . Such divergence may be an artifact of the calculations (too small a basis set) or it may indicate that the radius of convergence of  $1/Z$  expansions diminishes so rapidly with increasing  $N$  as to render this approach useless after only a modest increase in  $N$ ; indeed, for physical reasons, one tends to anticipate the latter. The primary motivation of this paper is to study the influence of  $N$  on the radius of convergence of the  $1/Z$  expansions, as well as the related issue of how screening<sup>16-18,6-8,36</sup> the nucleus may compensate for the unfavorable effect of increasing  $N$ . Evidently, a quantitative study of these issues requires accurate methods of evaluating the radii of convergence of the RS perturbation expansions. At present, numerical analysis of perturbation-expansion data offers the most accurate possibility of determining radii of convergence. Unfortunately, it is characteristic of numerical approaches that their accuracy depends upon the availability of quite high-order data to reduce the uncertainty of extrapolation to infinite order; this limits their application to special situations. The requisite input for such analysis is available<sup>20,21</sup> for a number of states of the  $N=2$  sequence, and accurate values of the radii of convergence of the  $1/Z$  expansions of some of these states have been determined by several numerical methods<sup>37</sup>; for  $N > 2$ , it appears, however, that one must resort to other methods until somewhat higher-order  $1/Z$  expansions have been made available.

To investigate  $1/Z$  or other types of RS expan-

sions for larger  $N$ , it would be useful to have a method for obtaining reasonably accurate estimates of radii of convergence from low-order data. Then, one would be able to determine the feasibility of a given RS perturbation approach in an almost *a priori* manner. In the present exploratory study, some progress is made towards this goal by developing a first-order procedure, based on a simple theoretical model, for obtaining improved estimates of RS radii of convergence. The requisite input essentially consists only of the RS first-order eigenfunction  $\psi_1$ ; by a slight approximation, the requirement of knowledge of  $\psi_1$  can be replaced by the less stringent one of knowledge of its norm  $\|\psi_1\|$ . The procedure is applicable to arbitrary stationary states of *all* systems described by *any* Hamiltonian linear in a real perturbing parameter, e.g., the  $1/Z$ -transformed<sup>10</sup> nonrelativistic Hamiltonian of atomic isoelectronic sequences. Thus, while our results pertain to  $1/Z$  expansions, they are not restricted to them. In the specific case of atomic isoelectronic sequences, the influence of screening<sup>6-8,16-18,36</sup> on the inverse-nuclear-charge expansions<sup>38</sup> is investigated, and it is shown how the radius of convergence is maximized within the framework of our model by an optimal choice of the screening parameter. In the event that  $\psi_1$  or  $\|\psi_1\|$  is not available, a modest estimate of the square norm  $\langle \psi_1 | \psi_1 \rangle$  suffices for the evaluation of the radius of convergence at the level of accuracy considered here; a simple method for obtaining such an estimate of the square norm is developed for both the unscreened and the optimally screened inverse-nuclear-charge expansions of atomic isoelectronic sequences.

In Sec. II, the theory is developed. In Sec. III, the procedure is tested and illustrated by application to the inverse-nuclear-charge expansions of several states of the  $2 \leq N \leq 10$  atomic isoelectronic sequences. Radii of convergence computed in this manner are critically compared to accurately known values and to other estimates. Optimal screening is then applied to the  $1/Z$  eigenvalue expansion of the  $1s^22s^2^1S$  state of the  $N=4$  sequence,<sup>26</sup> and the screened and unscreened total eigenvalues are compared over a range of  $Z$ . Finally, Sec. IV is devoted to a discussion of our results. The principal findings of this paper are as follows: (1) Our procedure leads to considerably improved estimates of the radii of convergence of  $1/Z$  expansions; (2) the effect of increasing  $N$  on the radii of convergence of the unscreened  $1/Z$  expansions is severe, e.g., for the ground states of the  $3 \leq N \leq 10$  sequences, the region of convergence is approximately limited to  $Z \geq 3N - 7$ ; and (3) optimal screening greatly increases the radii

of convergence of these expansions, and extends their applicability to at least  $N=10$ .

## II. THEORY

### A. Preliminaries

In this subsection, we summarize the necessary background for the present study. In a series of fundamental papers, Rellich,<sup>3</sup> and subsequently, Kato<sup>4,5</sup> have treated RS convergence in a rigorous manner. The relevant conclusions are as follows: Consider the perturbed time-independent Schrödinger equation

$$(H - \epsilon^{(s)})\psi^{(s)} = 0, \quad (1)$$

where  $H$  is the perturbed Hamiltonian, and  $\psi^{(s)}$  and  $\epsilon^{(s)}$  are, respectively, the perturbed exact normalized eigenfunction and eigenvalue of the  $s$ th stationary state; in what follows, we fix our attention on an arbitrary state and suppress the state superscript. Formally, the perturbation enters Eq. (1) in those cases when  $H$  can be treated as an operator-valued holomorphic function of a perturbing (coupling) parameter  $\lambda$ . The simplest  $H(\lambda)$  for which RS theory is applicable has the linear expansion

$$H = H(\lambda) = H_0 + H_1\lambda, \quad (2)$$

where  $H_0$  is the unperturbed Hamiltonian and  $H_1\lambda$  is the perturbing potential operator; this form is assumed throughout as it is sufficient to cover most applications<sup>2</sup> of RS theory. In the problems we consider, the physically significant values of  $\lambda$  are real but complex values cannot be excluded from consideration when studying convergence. In some cases,  $\lambda$  occurs naturally in  $H$  as the scalar measure of a physical quantity which governs the strength of  $H_1$ , while in certain other cases, a physically significant perturbing parameter  $\lambda$  can be introduced by a suitable transformation. Undoubtedly, the best known example of the latter is the  $1/Z$  scaling transformation<sup>10</sup> which brings the nonrelativistic Hamiltonian of an arbitrary  $N$ -electron atomic isoelectronic sequence into the form of Eq. (2), where in  $Z$ -scaled a.u. (unit of length  $Z^{-1}$  a.u., unit of energy  $Z^2$  a.u.),

$$H_0 = \sum_{i=1}^N h_0(i) = \sum_{i=1}^N \left(-\frac{1}{2} \Delta_i - r_i^{-1}\right), \quad (3a)$$

$$H_1 = \sum_{i < j}^N r_{ij}^{-1}, \quad (3b)$$

and the physically significant values of  $\lambda$  are

$$\lambda = Z^{-1} = 1, \frac{1}{2}, \frac{1}{3}, \dots \quad (3c)$$

Equations (3) represent the unscreened hydro-

genic partitioning of the Hamiltonian where the entire interelectronic repulsion, Eq. (3b), is taken as the perturbation. It is also useful to consider the screened<sup>16-18</sup> hydrogenic formulation for atomic isoelectronic sequences where a portion of the nuclear attraction potential is included in the perturbation. In  $Z'$ -scaled units [unit of length  $(Z')^{-1}$  a.u., unit of energy  $(Z')^2$  a.u.], this yields<sup>6-8,36</sup> the new Hamiltonian

$$H' = H'(\lambda') = H_0 + H_1\lambda', \quad (2')$$

where  $H_0$  is still given by Eq. (3a),

$$H_1' = \sum_{i < j}^N r_{ij}^{-1} - \sigma \sum_{i=1}^N r_i^{-1}, \quad (3b')$$

$$\lambda' = (Z')^{-1} \equiv (Z - \sigma)^{-1}, \quad (3c')$$

and  $\sigma$  is a disposable screening parameter; here and throughout, the prime denotes a quantity explicitly dependent upon  $\sigma$ . The unscreened and screened perturbed solutions to Eqs. (3) and (3') can thus be written as  $\psi(\vec{r}_1, \dots, \vec{r}_N)$ ,  $\epsilon$ , and  $\psi'(\vec{r}_1, \dots, \vec{r}_N)$ ,  $\epsilon'$ , respectively. In ordinary a.u., these are related<sup>8</sup> as follows:

$$Z^{3N/2} \psi(Z\vec{r}_1, \dots, Z\vec{r}_N) = (Z')^{3N/2} \psi'(Z'\vec{r}_1, \dots, Z'\vec{r}_N), \quad (4a)$$

$$Z^2 \epsilon = (Z')^2 \epsilon'. \quad (4b)$$

It was the significant contribution of Rellich, Kato, and others to derive sufficient conditions<sup>5</sup> for a given  $H(\lambda)$  to belong to a holomorphic family of operators, and hence, for the corresponding discrete state  $\psi(\lambda)$  and  $\epsilon(\lambda)$  to be holomorphic in a neighborhood of  $\lambda=0$ . Kato<sup>4(d),4(e)</sup> also proved that the commonly encountered Hamiltonians in atomic and molecular calculations for  $N$  particles interacting through pairwise Coulombic potentials, e.g., Eqs. (3) and (3'), were members of holomorphic families. For such operators, and for eigenstates where  $\epsilon_0$  is an isolated eigenvalue of  $H_0$  with finite multiplicity, one is assured that the RS expansions in powers of  $\lambda$ ,

$$\psi = \psi(\lambda) = \sum_{j=0}^{\infty} \psi_j \lambda^j, \quad (5a)$$

$$\epsilon = \epsilon(\lambda) = \sum_{j=0}^{\infty} \epsilon_j \lambda^j, \quad (5b)$$

exist and converge absolutely in the convergence circle  $|\lambda| < r_*$ , where  $r_*$  is the nonzero RS radius of convergence given by  $r_* = |\lambda_*|$ , and  $\lambda_*$  is the coordinate in the complex  $\lambda$  plane of the nearest singularity in  $\epsilon(\lambda)$  to the origin. For atomic isoelectronic sequences, Eqs. (5) represent the unscreened  $1/Z$  expansions,<sup>10-31</sup> which converge for

$Z > Z_*$  where  $Z_* = r_*^{-1}$ . Similarly, the screened  $1/Z'$  expansions<sup>6-8,36</sup> [cf. Eqs. (2') and (3')] for atomic isoelectronic sequences,

$$\psi' = \psi'(\lambda') = \sum_{j=0}^{\infty} \psi'_j(\lambda')^j, \quad (5a')$$

$$\epsilon' = \epsilon'(\lambda') = \sum_{j=0}^{\infty} \epsilon'_j(\lambda')^j, \quad (5b')$$

converge for  $|\lambda'| < r'_*$ , where  $r'_* = |\lambda'_*|$  and  $\lambda'_*$  locates the nearest singularity in  $\epsilon'(\lambda')$ . Given the  $\epsilon_j$ , Eq. (5b), one can calculate the  $\epsilon'_j$ , Eq. (5b'), for any value of  $\sigma$  satisfying  $|\sigma| < Z$  by the simple series transformation,<sup>17,18(a)</sup>

$$\epsilon'_0 = \epsilon_0, \quad (6a)$$

$$\epsilon'_1 = \epsilon_1 + 2\sigma\epsilon_0, \quad (6b)$$

$$\epsilon'_2 = \epsilon_2 + \sigma\epsilon_1 + \sigma^2\epsilon_0, \quad (6c)$$

$$\epsilon'_j = \sum_{i=0}^{j-3} \binom{j-3}{i} (-\sigma)^i \epsilon_{j-i}, \quad j=3, 4, \dots \quad (6d)$$

without the necessity of making actual calculations with the screened  $H'(\lambda')$ . It should be noted that although the artificially introduced  $\sigma$  dependency must cancel out of total eigenfunctions, eigenvalues, and other expectation values [as indicated in Eqs. (4)], a properly chosen  $\sigma$  may have considerable influence on the radius of convergence and, hence, on the comparative rates of convergence of the screened and unscreened RS expansions. This is not surprising since series transformation is a classical technique for accelerating convergence. Screening has been exploited by a number of authors<sup>6-8,16-18,36</sup> who used different criteria to fix the optimum  $\sigma$  for different purposes.

Ideally, the next step in the analysis would be the determination of  $\lambda_*$  for given systems. As is well known from the theory of complex functions,<sup>39</sup> evaluation of the modulus  $r_*$  is usually much simpler than determination of the location of the singularity  $\lambda_*$ . Thus, Rellich<sup>3</sup> and Kato<sup>4(d),5</sup> have shown how rigorous lower bounds  $r_{lb}$  to  $r_*$  can, in principle, be obtained in a general manner. Although of great theoretical significance in demonstrating convergence for nonzero  $r_*$ , these lower bounds have proved far too weak to be of much practical value. In the crucial example of the  $1/Z$  expansion for the ground state of the helium isoelectronic sequence, Kato<sup>4(d),7</sup> found that  $r_* \geq r_{lb} = 1/7.64 = 0.131$ ; evidently, it would be desirable to improve this estimate since it is one order of magnitude smaller than the numerically determined<sup>37</sup> presumably accurate value of  $r_* \approx 1.1-1.2$ , and can only assure convergence of the  $1/Z$  expansions for  $Z > Z_{\min} = 7.64$  (i.e., for  $O^{6+}$ ). Here,

from Eq. (3c), the estimated minimum nuclear charge  $Z_{\min}$  is given by

$$Z_{\min} = (r_{lb})^{-1}. \quad (7)$$

In earlier efforts to improve these lower bounds, two modifications of Kato's theory have been introduced, one based on optimizing the path of contour integration<sup>9</sup> and the other on the screening transformation,<sup>6-8</sup> Eq. (5'), for atomic isoelectronic sequences. On the basis of previous analysis,<sup>40</sup> it is not hard to show<sup>41</sup> that the former procedure is not very promising as it achieves only a negligible improvement in the estimate  $r_{lb}$  (which, again, is one order of magnitude too small) for the specific case considered of the ground state of a perturbed hydrogenic ion.<sup>9(a)</sup> On the other hand, Ahlrichs<sup>8</sup> has demonstrated by a refined calculation that screening is quite effective for the  $1/Z'$  expansion of the ground state of the helium isoelectronic sequence. By adjusting  $\sigma$  so as to maximize  $r'_{lb}$ , he found that  $\sigma = 0.34$ ,  $r'_* \geq r'_{lb} = 0.608$ , and  $Z > Z_{\min} = 1.98$ , thus for the first time assuring convergence for He. In the screened case, from Eq. (3c'),  $Z_{\min}$  is given by

$$Z_{\min} = (r'_{lb})^{-1} + \sigma. \quad (7')$$

Unfortunately, this lower-bound procedure is not effective for excited states of the helium isoelectronic sequence and for the lithium isoelectronic sequence to which it was also applied.<sup>8</sup> For example, for the  $1s^2 2s^2 S$  and  $1s^2 2p^2 P$  states of the lithium isoelectronic sequence, the unrealistically high value of  $Z_{\min} \approx 31.4$  was found while there is numerical evidence<sup>25(a)</sup> which indicates that even the unscreened  $1/Z$  expansions converge for at least  $Z \geq 5$ . In view of these difficulties, no estimates of  $Z_{\min}$  seem to be available for  $1/Z$  or  $1/Z'$  expansions of atomic isoelectronic sequences with  $N > 3$ . In the following two subsections, we present a new method for obtaining improved estimates of  $r_*$ , and in the special case of  $1/Z$  expansions, also of  $\sigma$ ,  $r'_*$ , and  $Z_{\min}$ . In principle, this procedure is applicable to all states of isoelectronic sequences with  $N \geq 2$ .

#### B. First-order estimation of $r_*$ and $r'_*$

Let  $\tilde{\psi}$  be an analytic but otherwise arbitrary ansatz to  $\psi$  for a given system and state which furnishes the variational approximation  $\tilde{\epsilon}$  to  $\epsilon$ ; throughout, the tilde denotes a trial function. In general,  $\tilde{\psi}$  may contain  $P$  adjustable variational parameters, the  $a_p$ , which occur linearly, nonlinearly, or in some combination. Then, depending upon the types<sup>42</sup> of variational parameters embedded in  $\tilde{\psi}$ , a number of different perturbational-variational (PV) methods are available<sup>43,22,44</sup> for

obtaining the stationary PV expansions,

$$\bar{a}_p = \bar{a}_p(\lambda) = \sum_{j=0}^{\infty} \bar{a}_{pj} \lambda^j, \quad p=1, 2, \dots, P \quad (8a)$$

$$\bar{\psi} = \bar{\psi}(\bar{a}_p) = \sum_{j=0}^{\infty} \bar{\psi}_j \lambda^j, \quad (8b)$$

$$\bar{\epsilon} = \bar{\epsilon}(\bar{a}_p; \lambda) = \frac{\langle \bar{\psi} | H(\lambda) | \bar{\psi} \rangle}{\langle \bar{\psi} | \bar{\psi} \rangle} = \sum_{j=0}^{\infty} \bar{\epsilon}_j \lambda^j; \quad (8c)$$

these converge for  $|\lambda| < \bar{r}_*$ , where  $\bar{r}_*$  is the non-zero PV radius of convergence given by  $\bar{r}_* = |\bar{\lambda}_*|$  and  $\bar{\lambda}_*$  locates the nearest singularity in  $\bar{\epsilon}(\lambda)$  to the  $\lambda$  origin. In general, the PV expansions, Eqs. (8), are variational counterparts to the exact RS expansions, Eqs. (5); all PV quantities are, of course, ansatz dependent. We adopt the normalization scheme for the RS and PV expansions with  $\psi_0$ ,  $\psi$ ,  $\bar{\psi}_0$ , and  $\bar{\psi}$  individually normalized, which yields

$$\sum_{j=0}^n \langle \psi_j | \psi_{n-j} \rangle = \delta_{n0}, \quad n=0, 1, \dots, \quad (9)$$

and an identical expression for the  $\bar{\psi}_j$ .

In order to gain insight into the convergence properties of the exact RS solutions for a given system and state, one can study corresponding PV expansions. Thus, in a number of cases, it has been found possible to determine<sup>45, 46, 40</sup> the PV  $\bar{\lambda}_*$  for selected  $\bar{\epsilon}(\lambda)$ . This approach has been intensively pursued by Stillinger and his colleagues<sup>46</sup> for PV  $1/Z$  expansions of atomic isoelectronic sequences using  $\bar{\psi}$  containing a small number of nonlinear variational parameters. Their purpose was to confirm Stillinger's<sup>37(a)</sup> conclusions concerning the convergence behavior of the RS  $1/Z$  eigenvalue expansion for the  $1s^2 1S$  state of the  $N=2$  sequence, and they indeed observed qualitatively similar behavior in a number of variational calculations for the  $N=2$  [Refs. 46(a) and 46(b)] and 10 [Ref. 46(c)] sequences.

The Wigner  $(2n+1)$  theorem<sup>2(b)</sup> implies that the RS eigenfunction expansion Eq. (5a) truncated after first order should be a fairly good approximation to the total eigenfunction, at least as far as the total eigenvalue is concerned. This has been confirmed numerically in a number of cases.<sup>18(a), 19, 28, 30, 47</sup> Thus, a natural and well-defined comparison  $\bar{\psi}$  to  $\psi$  is obtained by renormalizing the first-order expansion of  $\psi$ . This yields the well known expressions<sup>48</sup>

$$\bar{\psi}(1, \lambda) \equiv (1 + \langle \psi_1 | \psi_1 \rangle \lambda^2)^{-1/2} (\psi_0 + \psi_1 \lambda), \quad (10)$$

$$\bar{\epsilon}(1, \lambda) \equiv \langle \bar{\psi}(1, \lambda) | H_0 + H_1 \lambda | \bar{\psi}(1, \lambda) \rangle \\ = \sum_{j=0}^3 \epsilon_j \lambda^j - \frac{(\epsilon_2 \lambda^2 + \epsilon_3 \lambda^3) \langle \psi_1 | \psi_1 \rangle \lambda^2}{1 + \langle \psi_1 | \psi_1 \rangle \lambda^2}. \quad (11)$$

The PV eigenvalue expansion Eq. (8c) corresponding to Eq. (11) can be written as

$$\bar{\epsilon}_j = \epsilon_j, \quad j=0, 1, 2, 3 \quad (12a)$$

$$\bar{\epsilon}_j = -\langle \psi_1 | \psi_1 \rangle \bar{\epsilon}_{j-2}, \quad j=4, 5, \dots, \quad (12b)$$

where for lowest states, we have the upper bound

$$\bar{\epsilon}_4 = -\langle \psi_1 | \psi_1 \rangle \epsilon_2 \geq \epsilon_4. \quad (12c)$$

Now  $\bar{\epsilon}(1, \lambda)$ , Eq. (11), is a simple meromorphic function where the singularity  $\bar{\lambda}_*(1)$  limiting the convergence of Eqs. (12) is evidently

$$\bar{\lambda}_*(1) = \bar{r}_*(1) \exp\left(\pm i \frac{\pi}{2}\right), \quad (13a)$$

with radius of convergence  $\bar{r}_*(1)$  given by

$$\bar{r}_*(1) = \langle \psi_1 | \psi_1 \rangle^{-1/2} \equiv \|\psi_1\|^{-1}. \quad (13b)$$

We see that the first-order approximation to  $\lambda_*$  furnished by  $\bar{\epsilon}(1, \lambda)$  consists of two conjugated simple poles located on the imaginary  $\lambda$  axis with modulus given by  $\|\psi_1\|^{-1}$ . Note that if we were to examine  $\psi(1, \lambda)$ , Eq. (10), for its singularities, we would again find Eqs. (13) but with the distinction that the singularities are branch points of index  $-\frac{1}{2}$  corresponding to the fact that  $\bar{\psi}(1, \lambda)$  is a multivalued function. This provides a simple example of the previously discussed<sup>40</sup> possible difference in the nature of the singularities which, respectively, determine the radius of convergence of eigenfunction and eigenvalue expansions.

Qualitatively, Eq. (13b) makes good sense: One anticipates that the RS radius of convergence should vary inversely in some manner with the magnitude of the perturbation, and the latter is measured to a first approximation by the norm of the first-order eigenfunction. Quantitatively, however, one can only expect fairly crude results from this estimate. Although  $\bar{\epsilon}(1, \lambda)$  yields  $\epsilon(\lambda)$  correct through third order, it does suffer from the defect of not being stationary, and hence,  $\bar{\epsilon}(1, \lambda)$ , unlike  $\epsilon(\lambda)$ , does not satisfy the basic variational theorems, e.g., the Hellmann-Feynman,<sup>49</sup> virtual,<sup>50, 51</sup> and curvature<sup>52</sup> theorems. It has been shown<sup>40, 47</sup> that satisfaction of these variational theorems imposes severe constraints on the RS and PV eigenvalue expansions, and hence we infer, on their radii of convergence. In order to improve this first-order estimate of  $r_*$  without having to resort to high-order numerical analysis,<sup>37</sup> we adopt the simplest possible procedure of converting  $\bar{\psi}(1, \lambda)$  into a true variational ansatz by replacing<sup>53</sup>  $\lambda$  with an adjustable linear variational parameter  $c$ ; the resultant stationary eigenvalue will satisfy the Hellmann-Feynman theorem<sup>49(c)</sup> (for all states) and the curvature theorem<sup>52</sup> (for the lowest states). By conventional means,<sup>53, 54</sup> one obtains the sta-

tionary quantities

$$\bar{c} = \bar{c}(\lambda) = [\bar{\epsilon}(1, \bar{c}) - (\epsilon_0 + \epsilon_1 \lambda)] / \epsilon_2 \lambda, \quad (14a)$$

$$\bar{\psi}(1, \bar{c}) = (1 + \langle \psi_1 | \psi_1 \rangle \bar{c}^2)^{-1/2} (\psi_0 + \psi_1 \bar{c}), \quad (14b)$$

$$\bar{\epsilon}(1, \bar{c}) = \epsilon_0 + \epsilon_1 \lambda + \frac{\epsilon_2 - \epsilon_3 \lambda}{2 \langle \psi_1 | \psi_1 \rangle} [-1 + (1 + z)^{1/2}], \quad (15a)$$

$$z = z(\lambda) = 4 \langle \psi_1 | \psi_1 \rangle \epsilon_2^2 \lambda^2 / (\epsilon_2 - \epsilon_3 \lambda)^2, \quad (15b)$$

where the obvious notation distinguishes the  $\bar{c}$ -dependent quantities of Eqs. (14) and (15) from the corresponding ones of Eqs. (10) and (11) with  $c = \lambda$ . For  $|z| < 1$ , Eqs. (15) yield the PV eigenvalue expansion

$$\bar{\epsilon}_j(\bar{c}) = \epsilon_j, \quad j = 0, 1, 2, 3 \quad (16a)$$

$$\bar{\epsilon}_j(\bar{c}) = \left( \epsilon_3 \bar{\epsilon}_{j-1}(\bar{c}) - \langle \psi_1 | \psi_1 \rangle \sum_{k=2}^{j-2} \bar{\epsilon}_k(\bar{c}) \bar{\epsilon}_{j-k}(\bar{c}) \right) / \epsilon_2, \quad j = 4, 5, \dots, \quad (16b)$$

where for lowest states, we have the improved upper bound

$$\bar{\epsilon}_4(\bar{c}) = \epsilon_3^2 / \epsilon_2 - \langle \psi_1 | \psi_1 \rangle \epsilon_2 \geq \epsilon_4. \quad (16c)$$

Equations (12) and (16) should be compared and their different structure for  $j > 3$  noted. Clearly, from Eq. (15a), the singularity determining the convergence properties of the PV eigenvalue expansion of Eqs. (16) is a branch point of index  $\frac{1}{2}$  at  $z = -1$ . Substitution of this value of  $z$  into Eq. (15b) determines the corresponding singularity in  $\lambda$ ,  $\lambda_*(1, \bar{c})$ , as

$$\tilde{\lambda}_*(1, \bar{c}) = \tilde{r}_*(1, \bar{c}) \exp[\pm i \tan^{-1}(2 \|\psi_1\| \epsilon_2 / \epsilon_3)], \quad (17a)$$

with radius of convergence  $\tilde{r}_*(1, \bar{c})$  given by

$$\tilde{r}_*(1, \bar{c}) = |\epsilon_2| (4 \langle \psi_1 | \psi_1 \rangle \epsilon_2^2 + \epsilon_3^2)^{-1/2}. \quad (17b)$$

Now in those cases where accurate RS expansion data are available, one finds that  $4 \langle \psi_1 | \psi_1 \rangle \epsilon_2^2 \gg \epsilon_3^2$ ; whenever this is valid, one can expand Eq. (17b) to obtain

$$\begin{aligned} \tilde{r}_*(1, \bar{c}) &= \frac{1}{2} \|\psi_1\|^{-1} \left( 1 - \frac{\epsilon_3^2}{8 \langle \psi_1 | \psi_1 \rangle \epsilon_2^2} + \dots \right) \\ &\approx \frac{1}{2} \|\psi_1\|^{-1} = \frac{1}{2} \tilde{r}_*(1), \end{aligned} \quad (17c)$$

where the rhs follows from Eq. (13b). Further, in the special case of  $1/Z$  expansions of atomic isoelectronic sequences, Eq. (17c) yields the minimum nuclear charge

$$\tilde{Z}_{\min}(1, \bar{c}) = [\tilde{r}_*(1, \bar{c})]^{-1} \approx 2 \|\psi_1\|. \quad (18)$$

Note that the use of Eqs. (17c) and (18) only requires a knowledge of  $\|\psi_1\|$ . From Eq. (17a), we see that the variational improvement achieved in Eqs. (14) and (15) has converted the two conjugated simple poles of Eq. (13a) lying on the imaginary

$\lambda$  axis into two conjugated branch points lying slightly off the imaginary axis. It is of much greater interest, however, that the crude first-order estimate of the radius of convergence furnished by Eq. (13b) has been reduced by a factor of approximately one-half in Eq. (17c); this pronounced shift is even more striking when one considers that  $\bar{\epsilon}(1, \bar{c})$  demonstrates<sup>53</sup> only a slight *energetic* improvement over  $\bar{\epsilon}(1, \lambda)$ . Note also from Eqs. (17b) and (17c) that the effect of relatively larger magnitude of  $\epsilon_3$  is to reduce slightly the estimate of Eq. (17c), which is in accord with expectations. We put forth Eqs. (17b), (17c), and (18) as our best first-order estimates of  $r_*$  and  $Z_*$  for the unscreened  $1/Z$  expansions of atomic isoelectronic sequences; for brevity, we now simplify the notation and refer to the solutions of these equations as simply  $\tilde{r}_*$  and  $\tilde{Z}_{\min}$ .

All of the above results, Eqs. (8)–(18), are also applicable to the screened  $1/Z'$  expansions of atomic isoelectronic sequences upon replacing the unprimed quantities with their primed counterparts, and in the case of Eq. (18), making an additional obvious modification [cf. Eqs. (7) and (7')]. Thus, Eqs. (17b), (17c), and (18) become explicitly

$$\tilde{r}'_* = |\epsilon'_2| [4 \langle \psi'_1 | \psi'_1 \rangle (\epsilon'_2)^2 + (\epsilon'_3)^2]^{-1/2}, \quad (17b')$$

$$\tilde{r}'_* \approx \frac{1}{2} \|\psi'_1\|^{-1}, \quad (17c')$$

$$\tilde{Z}'_{\min} = (\tilde{r}'_*)^{-1} + \sigma \approx 2 \|\psi'_1\| + \sigma. \quad (18')$$

The screening parameter  $\sigma$  is still at our disposal, and may now be varied so as to maximize  $\tilde{r}'_*$  via Eq. (17b') or (17c'), or to minimize  $\tilde{Z}'_{\min}$  via Eq. (18'), each approach leading to a slightly different result for the optimum value  $\sigma_{\text{opt}}$ . In the simplest case, namely, the maximization of  $\tilde{r}'_*$  with Eq. (17c'), we immediately obtain

$$\frac{\partial \langle \psi'_1 | \psi'_1 \rangle}{\partial \sigma} = 0, \quad (19)$$

as the condition for determining  $\sigma_{\text{opt}}$ . Thus, to this order of approximation, one may maximize the screened radius of convergence by minimizing the square norm of  $\psi'_1$  with respect to the screening parameter. Drake and Dalgarno<sup>36(b)</sup> have considered Eq. (19) for a completely different purpose in the context of autoionizing resonances, and have shown how solutions for  $\sigma_{\text{opt}}$  may be obtained for the helium isoelectronic sequence. Since extension of their procedure to  $N > 2$  appears difficult, a simple method of estimating  $\sigma_{\text{opt}}$  via Eq. (19) for atomic isoelectronic sequences of arbitrary  $N$  is developed in the following subsection.

In practice, we have found (cf. Table II, Sec. III) that the estimates  $\tilde{r}_*$  obtained from Eqs. (17b) and (17c) differ but negligibly; similar remarks

apply to Eqs. (17b') and (17c'). Thus, in subsequent developments, we need only consider the simpler Eqs. (17c) and (17c').

### C. Estimation of $\langle \psi_1 | \psi_1 \rangle$ , $\sigma_{\text{opt}}$ , and $\langle \psi_1' | \psi_1' \rangle$

We present here a method for systematically estimating  $\langle \psi_1 | \psi_1 \rangle$ ,  $\sigma_{\text{opt}}$ , and  $\langle \psi_1' | \psi_1' \rangle$ , all of which are required in our procedure for studying the convergence of  $1/Z$  and  $1/Z'$  expansions of atomic isoelectronic sequences. Such approximate first-order data will enable us to examine convergence behavior in those cases where either  $\psi_1$  is not readily accessible or has not yet been computed. To obtain these estimates, we construct an ansatz  $\tilde{\psi}(a_p)$  to  $H(\lambda)$ , Eqs. (3), for each state and isoelectronic sequence of interest, and then generate the PV expansion of  $\tilde{\psi}$ , Eq. (8b), through first order by applying PV theory<sup>43</sup> to render the PV expansion of  $\tilde{\epsilon}$ , Eq. (8c), stationary through third order. Full details of the PV procedure are presented in the paper cited and need not be repeated here. This yields  $\tilde{\psi}_1$  whence we compute  $\langle \tilde{\psi}_1 | \tilde{\psi}_1 \rangle$ , and finally, via Eq. (19),  $\tilde{\sigma}_{\text{opt}}$ , and  $\langle \tilde{\psi}_1' | \tilde{\psi}_1' \rangle$ . Note that our goal differs from the usual one of obtaining an accurate third-order  $1/Z$  expansion of  $\epsilon$ ; we only require an adequate approximation to  $\langle \psi_1 | \psi_1 \rangle$ , and the quality of the  $\tilde{\epsilon}_j$  generated is immaterial.

Owing to the relative insensitivity of Eqs. (17c), (17c'), (18), and (18') to inaccuracies in the first-order eigenfunction, we anticipate that modest estimates of  $\psi_1$  should suffice. Thus, we assume that the independent-particle model is sufficiently accurate and construct the  $\tilde{\psi}(a_p)$  from a simple minimal-basis set of orthonormal atomic orbitals  $\chi_{nlms}$ . These we take in the usual form

$$\chi_{nlms} = R_{nl}(r; a_p) Y_{lm}(\theta, \phi) \begin{bmatrix} \alpha \\ \beta \end{bmatrix}, \quad (20)$$

where the normalized  $1s$ ,  $2s$ , and  $2p$  radial functions are, respectively, selected as the parameterized hydrogenic radial orbitals,

$$u \equiv R_{10} = 2k^{3/2} e^{-kr}, \quad (21a)$$

$$v \equiv R_{20} = (1 - \tau^2)^{-1/2} \left( \frac{(k\gamma)^{3/2}}{2\sqrt{2}} (2 - k\gamma r) e^{-k\gamma r/2} - \tau u \right), \quad (21b)$$

$$w \equiv R_{21} = \frac{(k\delta)^{5/2}}{2\sqrt{6}} r e^{-k\delta r/2}, \quad (21c)$$

and

$$\tau = \tau(\gamma) = 32\sqrt{2}\gamma^{3/2}(1 - \gamma)(2 + \gamma)^{-4}. \quad (22)$$

Here,  $k$ ,  $\gamma$ , and  $\delta$  are nonlinear variational parameters,  $k$  is an overall scaling parameter which assures that the virial theorem<sup>50,51</sup> is satisfied, and  $\tau$  is chosen to orthogonalize  $u$  and  $v$ . This basis set, which approximates the corresponding

HF orbitals, suffices to describe the ground states as well as a number of low-lying excited states of the  $2 \leq N \leq 10$  isoelectronic sequences. The hydrogenic form of the orbitals is selected to force the proper asymptotic behavior<sup>19,43</sup> of  $\tilde{\psi}$  and  $\tilde{\epsilon}$  for small  $\lambda$  (large  $Z$ ). The appropriate single configuration  $\tilde{\psi}$  are constructed<sup>55</sup> from these atomic orbitals by means of the usual Slater determinants. In constructing the  $\tilde{\psi}$ , we have remained within the framework of the HF approximation by neglecting the zero-order degeneracy<sup>16,33(a)</sup> with other configurations of the same symmetry which arises for  $4 \leq N \leq 8$ . This is justifiable since trial calculations indicate that lifting this degeneracy has a negligible effect on our estimates of radii of convergence.

We can obtain the PV expansion of  $\tilde{\psi}$  by substituting the PV expansions of the radial orbitals

$$R_{nl}(\bar{a}_p) = \sum_{j=0}^{\infty} R_{nlj} \lambda^j, \quad (23)$$

into  $\tilde{\psi}$  and collecting terms of like powers of  $\lambda$ . Here, through first order,

$$R_{n10} = R_{nl}(\bar{a}_{p0}), \quad (24a)$$

$$R_{n11} = \sum_p \bar{a}_{p1} \left( \frac{\partial R_{nl}(a_{p0})}{\partial a_{p0}} \right)_{\bar{a}_{p0}}, \quad (24b)$$

where the optimum  $\bar{a}_{p0}$  and  $\bar{a}_{p1}$  [cf. Eq. (8a)] for the various states and sequences in question have been analytically determined by the PV procedure.<sup>43</sup> Owing to the hydrogenic form of the orbitals, it follows that

$$\bar{k}_0 = \bar{\gamma}_0 = \bar{\delta}_0 = 1, \quad (25)$$

whence Eqs. (21) and (24a) yield

$$u_0 = 2e^{-r}, \quad (26a)$$

$$v_0 = \frac{1}{2\sqrt{2}} (2 - r) e^{-r/2}, \quad (26b)$$

$$w_0 = \frac{1}{2\sqrt{6}} r e^{-r/2}, \quad (26c)$$

$$\tilde{\psi}_0 = \tilde{\psi}_0^{\text{HF}}, \quad (27a)$$

$$\tilde{\epsilon}_0 = \epsilon_0, \quad (27b)$$

$$\tilde{\epsilon}_1 = \tilde{\epsilon}_1^{\text{HF}}. \quad (27c)$$

As indicated in Eqs. (27), our minimal-basis set necessarily yields results in agreement with HF calculations through zero order in the eigenfunction and first order in the eigenvalue. From Eqs. (21), (22), and (24b), the first-order radial orbitals are explicitly

$$u_1 = \bar{k}_1 (3 - 2r) e^{-r}, \quad (28a)$$

$$v_1 = \frac{\bar{k}_1 + \bar{\gamma}_1}{4\sqrt{2}} (6 - 7r + r^2) e^{-r/2} + \frac{64\sqrt{2}\bar{\gamma}_1}{81} e^{-r}, \quad (28b)$$

$$w_1 = \frac{\bar{k}_1 + \bar{\delta}_1}{4\sqrt{6}} (5r - r^2) e^{-r/2}. \quad (28c)$$

It is now a simple matter to compute  $\langle \bar{\psi}_1 | \bar{\psi}_1 \rangle$  for each state and sequence of interest. In terms of radial integrals, we obtain the following results:

$$1s2s^1S, \langle \bar{\psi}_1 | \bar{\psi}_1 \rangle = \langle u_1 | u_1 \rangle + \langle v_1 | v_1 \rangle \pm 2\langle u_0 | v_1 \rangle^2, \quad (29a)$$

where the plus sign refers to the singlet<sup>56</sup> and the minus sign to the triplet;

$$1s2p^1P, \langle \bar{\psi}_1 | \bar{\psi}_1 \rangle = \langle u_1 | u_1 \rangle + \langle w_1 | w_1 \rangle, \quad (29b)$$

$$2p^2P, \langle \bar{\psi}_1 | \bar{\psi}_1 \rangle = 2\langle w_1 | w_1 \rangle, \quad (29c)$$

$$1s^22s^2P, \langle \bar{\psi}_1 | \bar{\psi}_1 \rangle = 2\langle u_1 | u_1 \rangle + a(\langle v_1 | v_1 \rangle - 2\langle u_0 | v_1 \rangle^2) + b\langle w_1 | w_1 \rangle, \quad (29d)$$

where  $a=0, 1, 2$ , and  $b=0, 1, \dots, 6$ . All integrals are elementary and, hence, are not presented explicitly. Note that Eqs. (29) are a consequence of the orthonormality of the orbitals and are independent of our particular choice of  $u$ ,  $v$ , and  $w$ .

To determine  $\bar{\sigma}_{\text{opt}}$ , it appears that we would first have to reoptimize each ansatz, now denoted as  $\bar{\psi}'(\alpha'_p)$ , with respect to the screened  $H'(\lambda')$ , Eqs. (3'), for an arbitrary value of  $\sigma$ . It follows, however, from consideration of Eqs. (4) that for all optimized variational parameters,  $\bar{\alpha}_p = \bar{\alpha}'_p$  with the sole exception of the overall scaling parameter. In ordinary a.u., in analogy with Eqs. (4),

the optimized unscreened and screened scaling parameters are related by

$$Z\bar{k} = Z'\bar{k}'. \quad (30)$$

Insertion of the PV expansions of  $\bar{k}$  (in powers of  $\lambda$ ) and of  $\bar{k}'$  (in powers of  $\lambda'$ ) into Eq. (30) yields, through first order,

$$\bar{k}'_0 = \bar{k}_0 = 1, \quad (31a)$$

$$\bar{k}'_1 = \bar{k}_1 + \sigma, \quad (31b)$$

where  $\sigma$  is still at our disposal. Thus, Eqs. (29) for  $\langle \bar{\psi}_1 | \bar{\psi}_1 \rangle$  also apply to  $\langle \bar{\psi}'_1 | \bar{\psi}'_1 \rangle$  upon replacing  $u_1$ ,  $v_1$ ,  $w_1$ , Eqs. (28), with  $u'_1$ ,  $v'_1$ ,  $w'_1$ , where the latter screened orbitals differ only from the former unscreened ones in that  $\bar{k}_1$  has been replaced with  $\bar{k}_1 + \sigma$  in accordance with Eq. (31b). Evidently, the resultant expressions for  $\langle \bar{\psi}'_1 | \bar{\psi}'_1 \rangle$  are simple quadratic functions of  $\sigma$  which can be minimized analytically via Eq. (19) to yield  $\bar{\sigma}_{\text{opt}}$ .

### III. APPLICATIONS AND RESULTS

As a first test of our procedure, Eqs. (17b), (17c), and (18) were applied to the unscreened  $1/Z$  expansions of the ground and several excited states of the  $N=2$  and 3 isoelectronic sequences where accurate RS input data are available, and/or the radii of convergence have been previously calculated or estimated by other means. In Table I the requisite RS data are collected; also presented are the corresponding PV  $\langle \bar{\psi}_1 | \bar{\psi}_1 \rangle$  computed with Eqs. (29), and for comparison, the PV  $\bar{\epsilon}_2$ , all calculated with the minimal-basis set of Eqs.

TABLE I. RS and PV  $1/Z$  perturbation-expansion data (in  $Z^2$  a.u.) for several states of the helium and lithium isoelectronic sequences.

$N$	State	$-\epsilon_2^a$	$\epsilon_3^b$	$\langle \psi_1   \psi_1 \rangle^c$	$\langle \bar{\psi}_1   \bar{\psi}_1 \rangle^d$	$-\bar{\epsilon}_2^d$
2	$1s^21S$	0.157 666 4	0.008 699 0 <sup>e</sup>	0.239 869 5	0.146 484 38	0.097 656 25
	$1s2s^1S$	0.114 509 5	0.009 224 0	1.469 479 5	1.160 268 53	0.150 226 13 <sup>f</sup>
	$1s2s^3S$	0.047 409 3	-0.004 872 7	0.488 630 9	0.316 725 66	0.039 595 72
	$1s2p^1P$	0.157 028 5	0.026 059 6	1.474 356 4	1.463 351 31	0.146 383 05
	$1s2p^3P$	0.072 998 9	-0.016 594 3	0.740 833 3	0.645 610 98	0.065 471 52
	$2p^2P$	0.039 394 7 <sup>e</sup>	0.001 840 0 <sup>e</sup>	0.394 617 5	0.269 165 04	0.026 916 50
3	$1s^22s^2S$	0.408 165 2 <sup>g</sup>	-0.016 55 <sup>h</sup>		1.991 964 32	0.319 087 77
	$1s^22p^2P$	0.528 578 6 <sup>g</sup>	-0.07 <sup>i</sup>		3.449 027 74	0.445 815 03

<sup>a</sup> Unless otherwise indicated, see Ref. 30(a).

<sup>b</sup> Unless otherwise indicated, see Ref. 21(c).

<sup>c</sup> These values of  $\langle \psi_1 | \psi_1 \rangle$ , computed with 140- to 168-term bases, were kindly supplied by Professor J. Midtdal, Ref. 57.

<sup>d</sup> Present calculation; unscreened PV expansions computed with minimal-basis set.

<sup>e</sup> Reference 20.

<sup>f</sup> Not an upper bound to  $\epsilon_2$  since the requisite orthogonality conditions have not been imposed; see Ref. 56.

<sup>g</sup> Reference 28(c).

<sup>h</sup> Reference 28(d).

<sup>i</sup> Estimate, Ref. 28(b).



TABLE II. Comparison of estimates and more accurate values of RS radii of convergence of  $1/Z$  perturbation expansions for several states of the helium and lithium isoelectronic sequences.

$N$	State	Eq. (17b) <sup>a</sup>	$\tilde{r}_*$ Eq. (17c) <sup>b</sup>	$r_*$ <sup>c</sup>	$\bar{Z}_{\min}$ Eq. (18) <sup>b</sup>	$Z_*$ <sup>c,d</sup>	$Z_{\min}$ <sup>e</sup>
2	$1s^2^1S$	1.019	1.021	1.118 <sup>f</sup>	0.98	0.894 <sup>f</sup>	1.98
			1.306		0.77		
	$1s2s^1S$	0.412	0.412	0.835	2.43	1.197	24.6
			0.464		2.15		
	$1s2s^3S$	0.713	0.715	0.925	1.40	1.082	6.6
			0.888		1.13		
	$1s2p^1P$	0.411	0.412	0.777	2.43	1.286	13.2
		0.413		2.42			
$1s2p^3P$	0.576	0.581	0.758	1.74	1.319	6.6	
		0.622		1.61			
		0.796	1.013 <sup>f</sup>	1.26	0.987 <sup>f</sup>	5.0	
		0.964		1.04			
3	$1s^22s^2S$		0.354		2.82		31.4
	$1s^22p^2P$		0.269		3.71		31.4

<sup>a</sup> Present calculation; computed with accurate RS input data from Table I.

<sup>b</sup> Present calculation; for each state, the first entry is computed with the appropriate RS  $\|\psi_1\|$  from Table I and the second entry with the appropriate PV  $\|\tilde{\psi}_1\|$ .

<sup>c</sup> Most accurate values available, computed by numerical analysis of high-order data; unless otherwise indicated, see Ref. 37(b).

<sup>d</sup>  $Z_* \equiv r_*^{-1}$ .

<sup>e</sup> Theoretical lower bounds to the minimum nuclear charge [cf. Eqs. (7) and (7')] via Kato's procedure, Ref. 8; other lower bounds for the ground state of the helium isoelectronic sequence are 7.64 [Ref. 4(d)], 4.07 (Ref. 7), and 3.53 (Ref. 8).

<sup>f</sup> Reference 37(a).

(20)–(22). For these same states and sequences, Table II displays the values of  $\tilde{r}_*$  computed with both Eqs. (17b) and (17c) using the accurate RS expansion data, as well as  $r_*$  computed with Eq. (17c) using the PV  $\langle\tilde{\psi}_1|\tilde{\psi}_1\rangle$ ; the corresponding values of  $\bar{Z}_{\min}$  computed with Eq. (18) are also tabulated. Further, in Table II the most accurate

values of  $r_*$  and  $Z_*$  are collected, as well as the best lower-bound estimates  $Z_{\min}$ .

To prepare the way for extension of the procedure to larger  $N$ , the minimal-basis set was used to calculate the unscreened  $\langle\tilde{\psi}_1|\tilde{\psi}_1\rangle$ ,  $\tilde{\sigma}_{\text{opt}}$ , and the optimally screened  $\langle\tilde{\psi}'_1|\tilde{\psi}'_1\rangle$  for the ground states of the  $3 \leq N \leq 10$  isoelectronic sequences and for

TABLE III. Unscreened ( $1/Z$ ) and optimally screened ( $1/Z'$ ) PV expansion data for the  $3 \leq N \leq 10$  atomic isoelectronic sequences.

$N$	State	$-\epsilon_2$ <sup>a</sup>	$-\tilde{\epsilon}_2$ <sup>b</sup>	$\langle\tilde{\psi}_1 \tilde{\psi}_1\rangle$ <sup>b</sup>	$\tilde{\sigma}_{\text{opt}}$ <sup>c</sup>	$\langle\tilde{\psi}'_1 \tilde{\psi}'_1\rangle$ <sup>d</sup>
3	$1s^22s^2S$	0.408 165	0.319 088	1.991 964 32	0.727 918 791	0.335 760 289
	$1s^22p^2P$	0.528 579	0.445 815	3.449 027 74	0.923 231 515	1.105 047 558
4	$1s^22s^2^1S$	0.881 945	0.716 604	5.287 030 66	0.999 853 938	0.537 008 714
5	$1s^22s^22p^2P$	1.856 650	1.552 076	13.075 888 69	1.373 089 407	1.760 983 484
6	$1s^22s^22p^2^3P$	3.288 002	2.807 918	24.986 529 77	1.730 772 566	3.264 397 337
7	$1s^22s^22p^3^4S$	5.264 012	4.564 878	41.826 449 01	2.079 763 590	5.054 309 830
8	$1s^22s^22p^4^3P$	8.131 865	7.070 946	66.075 533 42	2.450 444 484	7.521 455 584
9	$1s^22s^22p^5^2P$	11.755 106	10.275 908	97.231 641 06	2.811 454 824	10.273 436 74
10	$1s^22s^22p^6^1S$	16.272 878	14.259 678	136.093 924 4	3.165 754 643	13.310 264 76

<sup>a</sup> RS values (in  $Z^2$  a.u.) included for comparison; Ref. 30(a).

<sup>b</sup> Present calculation; unscreened PV expansion (in  $Z^2$  a.u.) computed with minimal-basis set.

<sup>c</sup> Optimal screening parameter computed from Eq. (19) using PV  $\langle\tilde{\psi}'_1|\tilde{\psi}'_1\rangle$ .

<sup>d</sup> Screened minimized PV values [in  $(Z')^2$  a.u.] calculated with  $\tilde{\sigma}_{\text{opt}}$ .

TABLE IV. Estimates<sup>a</sup> of radii of convergence of unscreened ( $1/Z$ ) and optimally screened ( $1/Z'$ ) perturbation expansions for the  $3 \leq N \leq 10$  atomic isoelectronic sequences.

$N$	State	$\tilde{r}_*$ <sup>b</sup>	$\tilde{Z}_{\min}$ <sup>c</sup>	$\tilde{r}'_*$ <sup>d</sup>	$\tilde{Z}'_{\min}$ <sup>e</sup>
3	$1s^2 2s^2 S$	0.354	2.82	0.827	1.89
	$1s^2 2p^2 P$	0.269	3.71	0.476	3.03
4	$1s^2 2s^2 1S$	0.217	4.60	0.682	2.47
5	$1s^2 2s^2 2p^2 P$	0.138	7.23	0.377	4.03
6	$1s^2 2s^2 2p^2 3P$	0.100	10.00	0.277	5.34
7	$1s^2 2s^2 2p^3 4S$	0.0773	12.93	0.222	6.58
8	$1s^2 2s^2 2p^4 3P$	0.0615	16.26	0.182	7.94
9	$1s^2 2s^2 2p^5 2P$	0.0507	19.72	0.156	9.22
10	$1s^2 2s^2 2p^6 1S$	0.0429	23.33	0.137	10.46

<sup>a</sup> All computations made with requisite PV unscreened and optimally screened expansion data of Table III.

<sup>b</sup> Unscreened, Eq. (17c).

<sup>c</sup> Unscreened, Eq. (18).

<sup>d</sup> Screened, Eq. (17c').

<sup>e</sup> Screened, Eq. (18').

the  $1s^2 2p^2 P$  state of the  $N=3$  sequence. The resultant PV expansion data are collected in Table III which also displays the corresponding RS  $\epsilon_2$  and PV  $\tilde{\epsilon}_2$  for comparison. The PV data for these states and sequences were then used to calculate the unscreened  $\tilde{r}_*$  and  $\tilde{Z}_{\min}$  via Eqs. (17c) and (18), respectively, for the  $1/Z$  expansions, and, analogously, the optimally screened  $\tilde{r}'_*$  and  $\tilde{Z}'_{\min}$  via Eqs. (17c') and (18'), for the  $1/Z'$  expansions. Table IV presents these results.

Finally, to verify our theoretical findings concerning the effect of optimal screening on the radius of convergence, the optimal screening procedure was numerically applied to the tenth-order unscreened  $1/Z$  eigenvalue expansion for the  $1s^2 2s^2 1S$  state of the  $N=4$  isoelectronic sequence

TABLE V. Unscreened ( $1/Z$ ) and optimally screened ( $1/Z'$ ) eigenvalue expansion coefficients for the  $1s^2 2s^2 1S$  state of the beryllium isoelectronic sequence.

$j$	$\epsilon_j$ <sup>a</sup>	$\epsilon'_j$ <sup>b</sup>
0	-1.250.000 00	-1.250 000 00
1	1.559 274 21	-0.940 360 637
2	-0.852 393 349	-0.542 981 764
3	-0.079 065 343 8	-0.079 065 343 8
4	0.042 664 244 6	0.121 718 040
5	0.190 961 545	0.026 603 270 4
6	3.852 019 09	3.486 204 18
7	12.892 919 5	-1.617 073 11
8	3.830 020 30	-23.732 796 9
9	-84.422 408 6	11.459 454 4
10	-334.899 136	16.435 885 9

<sup>a</sup> Unscreened ( $Z^2$  a.u.); Ref. 26.

<sup>b</sup> Optimally screened [ $(Z')^2$  a.u.]; computed with Eqs. (6) and  $\tilde{\sigma}_{\text{opt}}$ , Table III.

previously computed by Watson and O'Neil.<sup>26</sup>

The optimally screened  $\epsilon'_j$  for the  $1/Z'$  expansion were obtained from the unscreened  $\epsilon_j$  with Eqs. (6) using the appropriate  $\tilde{\sigma}_{\text{opt}}$  from Table III; both sets of expansion coefficients are collected in Table V. Total eigenvalues were then computed for the range of  $3 \leq Z \leq 8$  by summation of the tenth-order optimally screened  $1/Z'$  expansion. The tenth-order unscreened and screened eigenvalue summations for these  $Z$  values are presented in Table VI where they are compared with the accurate configuration-interaction (CI) calculations of Weiss.<sup>58(a)</sup>

#### IV. DISCUSSION AND CONCLUSIONS

A number of interesting features emerge from a study of the results reported in Table II for the unscreened  $1/Z$  expansions of the helium and lithium isoelectronic sequences. First consider the helium sequence where the widest range of comparisons is possible amongst the various types of calculations:

(1) As previously mentioned, Eq. (17c) is such an excellent approximation to Eq. (17b) that we can adopt the former simpler expression as defining the estimate  $\tilde{r}_*$ .

(2) Of equal significance is the fact that the estimates  $\tilde{r}_*$  computed from Eq. (17c) using either the RS  $\|\psi_i\|$  or the PV  $\|\tilde{\psi}_i\|$  (cf. Table I) are in quite good agreement despite the simplicity of the trial eigenfunctions  $\tilde{\psi}$  used. This tends to confirm our assumption that modest estimates of  $\psi_i$  are sufficient, and encourages us to proceed to larger  $N$ .

(3) The agreement between the estimates  $\tilde{Z}_{\min}$  and the most accurate values of  $Z_*$  (or between  $\tilde{r}_*$  and  $r_*$ ) is striking. In practical terms, the maximum deviation between  $\tilde{Z}_{\min}$  and  $Z_*$  is only one unit of nuclear charge. Thus, for the  $1s^2 1S$ ,  $1s 2s^3 S$ , and  $1s 2p^3 P$  states, Eq. (18) predicts convergence for  $Z \geq 1$ ,  $Z \geq 2$ , and  $Z \geq 2$ , respectively, in harmony with the accurate numerical results from high-order expansions<sup>20,21,37</sup>; for the  $1s 2s^1 S$ ,  $1s 2p^1 P$ , and  $2p^2 3P$  states, the predictions of Eq. (18) are convergence for  $Z \geq 3$ ,  $Z \geq 3$ , and  $Z \geq 2$ , respectively, which are each one unit higher than the accurate numerically obtained values.

(4) Although there is no theoretical basis at present, all estimates  $\tilde{r}_*$  from Eq. (17c) are lower bounds to  $r_*$  with one exception,  $\tilde{r}_* = 1.306$  for the  $1s^2 1S$  state, computed with the PV  $\|\tilde{\psi}_1\|$ . One may argue that in this case, the  $\tilde{\psi}$  used is a particularly crude ansatz as it is simply the one-parameter variationally scaled  $\psi_0$ , and hence, is inadequate because of the large correlation energy for the ground state. If one uses instead the

TABLE VI. Comparison of summation of  $1/Z$  and  $1/Z'$  eigenvalue expansions with total variational eigenvalues for the  $1s^2s^2^1S$  state of the beryllium isoelectronic sequence (in a.u.).

$Z$	$Z^2\epsilon^a$	$\Delta E_1^b$	$(Z')^2\epsilon'^c$	$\Delta E_2^d$	$E_{CI}^e$	$\Delta E_1 + \Delta E_2$
3	-7.4229	-0.0572	-7.4801	-0.0155	-7.4956	-0.0727
4	-14.6111	-0.0045	-14.6156	-0.0453	-14.6609	-0.0498
5	-24.3099	-0.0007	-24.3106	-0.0307	-24.3413	-0.0314
6	-36.5036	-0.0001	-36.5037	-0.0225	-36.5262	-0.0226
7	-51.1951	0.0000	-51.1951	-0.0177	-51.2128	-0.0177
8	-68.3858	0.0000	-68.3858	-0.0143	-68.4001	-0.0143

<sup>a</sup> Unscreened summation, Ref. 26:  $Z^2\epsilon = Z^2\epsilon_0 + Z\epsilon_1 + \dots + Z^{-8}\epsilon_{10}$ ; cf. Table V.

<sup>b</sup>  $\Delta E_1 = (Z')^2\epsilon' - Z^2\epsilon$ .

<sup>c</sup> Optimally screened summation, present calculation:  $(Z')^2\epsilon' = (Z')^2\epsilon'_0 + Z'\epsilon'_1 + \dots + (Z')^{-8}\epsilon'_{10}$ ; cf. Table V.

<sup>d</sup>  $\Delta E_2 = E_{CI} - (Z')^2\epsilon'$ .

<sup>e</sup> Configuration-interaction calculations, Ref. 58(a).

open-shell ( $1s1s'$ ) Hylleraas<sup>59</sup>-Eckart<sup>60</sup> two-parameter ansatz, one easily obtains via PV analysis,<sup>43</sup>  $\langle \bar{\psi}_1 | \bar{\psi}_1 \rangle = \frac{948}{4096} = 0.231445312$  whence Eq. (17c) yields the lower bound of  $\tilde{r}_* = 1.039$ . Certainly, however, the initial value of  $\tilde{r}_*$  is entirely satisfactory.

(5) Finally, comparison of  $\tilde{Z}_{\min}$  computed with Eq. (18) and the best<sup>8</sup> lower bounds  $Z_{\min}$  obtained with Kato's technique reveals the advantages of our approach. The latter are larger than our estimates by factors ranging from two (in the case of the most refined Kato-type lower-bound calculation for the  $1s^2^1S$  state) to ten (for the  $1s2s^1S$  state).

Now consider the lithium isoelectronic sequence. Since the RS  $\|\psi_i\|$  are not readily accessible, we have contented ourselves with the PV  $\|\bar{\psi}_1\|$ . For the  $1s^22s^2^2S$  and  $1s^22p^2^2P$  states, as shown in Table II, Eq. (18) predicts convergence for  $Z \geq 3$  and 4, respectively, whereas the weak Kato-type lower bound can only assure convergence for  $Z \geq 32$  for both states. Although accurate values of  $Z_*$  do not seem to be available for comparison, the eighth-order  $1/Z$  eigenvalue expansions of Onello, Ford, and Dalgarno<sup>25(a)</sup> for these states, are in harmony with our findings. Thus, for  $Z = 3$  and 4, summation of the  $1/Z$  eigenvalue expansion for the  $1s^22s^2^2S$  state yields, respectively, the eigenvalues  $-7.46962$  a.u. ( $-0.00748$  a.u.) and  $-14.32005$  a.u. ( $-0.00345$  a.u.) and, analogously, for the  $1s^22p^2^2P$  state,  $-7.37956$  a.u. ( $-0.02882$  a.u.) and  $-14.16995$  a.u. ( $-0.00471$  a.u.); here, the numbers in parentheses give the superiority of accurate CI calculations<sup>58</sup> for these states and  $Z$  values over the summations. Note that for  $Z = 3$ , the error in the summation for the  $1s^22p^2^2P$  state is about four times larger than for the  $1s^22s^2^2S$  state indicating divergence of the former, while for  $Z = 4$ , the errors for both states have

diminished considerably and differ but slightly. We interpret these results as bearing out our predictions.

The estimates of radii of convergence collected in Table IV graphically illustrate the drastic influence of increasing  $N$  on the convergence of the unscreened  $1/Z$  expansions. Thus, for the  $1s^22s^2^2S$  state of the beryllium isoelectronic sequence, Eq. (18) predicts convergence of the  $1/Z$  expansion for  $Z \geq 5$ , in exact agreement with the numerically observed<sup>26</sup> behavior. The radii of convergence then continue to diminish so rapidly that, for example, for the ground states of the oxygen and neon isoelectronic sequences, convergence of the  $1/Z$  expansions is, respectively, predicted for the large values of  $Z \geq 17$  and  $Z \geq 24$ . For  $3 \leq N \leq 10$ , these estimates can be expressed approximately as convergence for  $Z \geq 3N - 7$ . All of these results are in accord with physical expectations based on the rapidly increasing strength of the perturbation, Eq. (3b), with increasing  $N$ . The only other estimate of a radius of convergence of  $1/Z$  expansions for larger  $N$  appears to be that of Herrick and Stillinger<sup>46(c)</sup> for the ground state of the neon isoelectronic sequence. These authors found  $\tilde{r}_* = 0.1185$  and  $0.1167$  (equivalent to  $\tilde{Z}_{\min} = 8.44$  and  $8.57$ ) by numerically examining total variational eigenvalues  $\tilde{\epsilon}$  for their singularities without actually obtaining the PV  $1/Z$  expansions. Although, no doubt, their estimate of convergence for  $Z \geq 9$  holds for the PV  $1/Z$  expansions of the  $\tilde{\epsilon}$  specifically studied, it seems entirely too low to apply to more accurate RS  $1/Z$  expansions for the neon isoelectronic sequence; quite apart from the present calculation, one would arrive at the latter conclusion from the previously described convergence behavior of the  $1/Z$  expansions of the lithium<sup>25(a)</sup> and beryllium<sup>26</sup> isoelectronic sequences.

The influence of optimal screening in compensating for the effects of increasing  $N$  is also shown in Table IV. Thus for the ground states it is predicted that the optimally screened  $1/Z'$  expansions, Eqs. (2'), (3'), and (5'), will converge for  $Z \geq 3$  for the beryllium isoelectronic sequence, for  $Z \geq N$  for the boron through oxygen isoelectronic sequences, and for  $Z \geq N+1$  for the fluorine and neon isoelectronic sequences. This extends the application of such expansions to at least  $N=10$ , and probably to still larger  $N$  for the study of the higher ionized members of the isoelectronic sequences. These results confirm the opinion advanced by Fröman and Hall<sup>6</sup> that screening was necessary to extend inverse-nuclear-charge expansions to sequences with larger  $N$ . Our findings also substantiate the semiempirical work of Edlén<sup>61</sup> and others<sup>18(a)</sup> who have long advocated the use of screening parameters for the accurate representation of the ionization potentials of atomic isoelectronic sequences.

Now we consider in somewhat greater detail the specific influence of optimal screening on the  $1/Z$  eigenvalue expansion for the  $1s^2 2s^2 1S$  state of the beryllium<sup>26</sup> isoelectronic sequence. Comparison of the  $\tilde{\sigma}_{opt}$  transformed  $\epsilon'_j$  and the unscreened  $\epsilon_j$  for this sequence and state presented in Table V demonstrates the smoothing effect of optimal screening in reducing the magnitude of the high-order expansion coefficients. In this connection, it is interesting to note that the  $\tilde{\sigma}_{opt}$ , computed via Eq. (19) and collected in Table III, are considerably larger than the  $\sigma$  selected so as to make  $\epsilon'_j$  vanish<sup>17</sup>; the latter, given by  $\sigma = -\epsilon_1/2\epsilon_0$  [cf. Eq. (6b)], range from 63% ( $N=3$ ) to 69% ( $N=10$ ) of the  $\tilde{\sigma}_{opt}$  for the ground states. Finally, we study the trend of the total eigenvalues shown in Table VI. The rapid increase of  $\Delta E_1 + \Delta E_2$  (which measures the superiority of the accurate<sup>58(a)</sup> CI eigenvalue  $E_{CI}$  over the unscreened summation) with decreasing  $Z$  between  $Z=5$  and 4 clearly supports the conclusion<sup>26</sup> that the  $1/Z$  expansion diverges for  $Z < 5$ . Now Weiss<sup>58(a)</sup> has observed exactly the reverse trend in his CI calculations for the  $N=2, 3$ , and 4 isoelectronic sequences, i.e., the  $E_{CI}$  increase in accuracy in reference to exact values with decreasing  $Z$ , displaying a sharp dip in error for  $Z < N$ . From this we infer that the intermediate- and higher-order eigenvalue perturbation-expansion coefficients implicit<sup>18(b)</sup> in the total variational eigenvalues  $E_{CI}$  make significant negative contributions for smaller  $Z$ . On the other hand, the eigenvalue perturbation expansions are subject to two opposing effects with decreasing  $Z$ ; one is the effect of truncation

which leads to increasing error, and the other is the aforementioned opposite effect of the increasing negative contributions of the intermediate expansion coefficients which are still retained in the truncated expansion. Such increasing negative contributions for decreasing  $Z$  are, of course, dependent upon remaining within the radius of convergence of the expansion. Thus for the unscreened  $1/Z$  summations, where one is outside the radius of convergence for  $Z < 5$ ,  $\Delta E_1 + \Delta E_2$  can only continue to grow monotonically with decreasing  $Z$  as demonstrated in Table VI. For the optimally screened  $1/Z'$  expansions, however, it is seen from Table VI that  $\Delta E_2$ , the error relative to  $E_{CI}$ , passes through a maximum at  $Z=4$  and decreases sharply for  $Z=3$ . This is precisely the behavior that one would anticipate if one were still within the radius of convergence for  $Z \geq 3$ . By the same arguments  $\Delta E_1$ , which measures the error in the unscreened summations relative to the screened ones, should display the same trend as  $\Delta E_1 + \Delta E_2$  and again this is observed. It follows that the results of Table VI quantitatively confirm our prediction that the optimal screening of the  $1/Z'$  eigenvalue expansion for this sequence and state should extend convergence to  $Z \geq 3$ .

On the basis of the supporting numerical evidence, it is concluded that the simple theoretical model of the radius of convergence presented in this paper reproduces the main features of the problem. In some cases, the extremely good agreement between the estimates and the accurately known values of the radii of convergence may be partly fortuitous. This requires further investigation with more accurate first-order eigenfunctions and with higher-order  $1/Z$  expansions for larger  $N$ . In this connection, it would be of great interest to seek analytical relationships between radii of convergence of isoelectronic sequences with  $N > 2$  and those of various states of the  $N=2$  sequence. This should be possible in view of the known relationship<sup>27</sup> between the first-order eigenfunctions of these sequences.

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- <sup>42</sup>For nonlinear variational parameters or a combination of nonlinear and linear parameters, the original PV linearization procedure of Ref. 43 is applicable; if all variational parameters are linear, as in a Rayleigh-Ritz (RR) ansatz, the modified HSK procedure of Ref. 22 or the closely related PV-RR method of Ref. 44 is best suited. Stationary values of the variational parameters and their PV expansions are denoted by superior bars; omission of the bars denotes arbitrary values.
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- <sup>48</sup>Reference 2(b), pp. 267 and 359; our notation differs slightly.
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- <sup>51</sup>For a discussion of the virial and other variational theorems in conjunction with perturbation theory, see P.-O. Löwdin, *J. Mol. Spectrosc.* **3**, 46 (1959), and Refs. 40, 43, 47, and 52.
- <sup>52</sup>J. N. Silverman and J. C. van Leuven, *Chem. Phys. Lett.* **7**, 37 (1970); **7**, 640 (1970).
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- <sup>54</sup>Reference 2(b), p. 311; there is a typographical error in Eq. (VI, 28).
- <sup>55</sup>For similar single-configuration calculations, but by conventional variational means, see C. C. J. Roothaan, Technical Report, Laboratory of Molecular Structure and Spectra, The University of Chicago, pp. 24–47, 1955 (unpublished); the minimal-basis set used there contained a Slater-type rather than a hydrogenic  $2s$  orbital.
- <sup>56</sup>For the  $1s2s \ ^1S$  state, our normalized ansatz can be written as  $\tilde{\psi} = (2)^{-1/2}(4\pi)^{-1}[u(1)v(2) + v(1)u(2)]$ , where we have omitted the conventional spin function. Evidently, substitution of  $u_0$  and  $v_0$  generates the exact  $\psi_0$ . It is not hard to show, however, that the PV  $\tilde{\psi}_1$  obtained from this ansatz via  $u_0, v_0, u_1$ , and  $v_1$  is not constrained to yield an upper bound to  $\epsilon_2$  because it is not suitably related to the zero-order eigenfunction of the  $1s^2 \ ^1S$  state. Essentially, this results from not allowing  $\tau$ , Eq. (22), to vary freely; see Refs. 12, and particularly the discussion in Ref. 12(c), as well as a related discussion in Ref. 14(a). Despite this variational shortcoming,  $\tilde{\psi}_1$  does yield an adequate approximation to  $\langle \psi_1 | \psi_1 \rangle$ .
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