and 4. Figure 3 is for $T = 90\,^{\circ}\mathrm{K}$ while Fig. 4 is for $300\,^{\circ}\mathrm{K}$ and the points marked represent the experimental data summarized in Sec. II. The dashed line in Fig. 4 is the value for ϵ_1 determined by the simple theory of dispersion forces which is in excellent agreement with most of the measurements.

The excellent agreement of these results with the resolved line data on linewidth magnitude, temperature, and quantum-number dependence indicates the importance of using a strong-collision model when large values of the phase integral are important. Straight-line perturber trajectories, series expansion of the scattering operator and impact parameter cutoffs are likely to be invalid approximations in such a case. Expansion of the scattering operator in spherical harmonics and the use of curved trajectories, while generally a more complicated procedure is straightforward and for the case of linear molecules, simple.

*Present address: Department of Physics and Astrophysics, University of Colorado, Boulder, Colo. 80302.

[1]T. A. Dillon, E. W. Smith, J. Cooper, and M. Mizushima, Phys. Rev. A 2, 1839 (1970).

[2]U. Fano, Phys. Rev. 131, 259 (1963). Note: In Fano's notation $i\Lambda = \langle n \rangle$.

[3]M. Baranger, Phys. Rev. 111, 502 (1958).

[4]M. W. P. Strandberg, *Microwave Spectroscopy* (Wiley, New York, 1954), pp. 75–80.

[5]M. Mizushima and R. M. Hill, Phys. Rev. 93, 745 (1954).

[6]G. Herzberg, *Spectra on Diatomic Molecules* (Van Nostrand, New York, 1950), p. 130.

[7]R. M. Hill and W. Gordy, Phys. Rev. 93, 1019 (1954).

[8]A. D. Buckingham, in *Advances in Chemical Physics XII*, edited by J. O. Herschfelder (Interscience, New York, 1967), pp. 107–142.

[9]J. O. Herschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 207.

[10]J. O. Herschfelder, R. B. Bird, and E. L. Spotz, J. Chem. Phys. 16, 968 (1948).

[11]R. W. Zimmerer and M. Mizushima, Phys. Rev. 121, 152 (1961).

[12]J. O. Artman and J. P. Gordon, Phys. Rev. 96, 1237 (1954).

[13]R. S. Anderson, W. V. Smith, and W. Gordy, Phys. Rev. 87, 561 (1952).

[14]B. V. Gokhale and M. W. P. Strandberg, Phys. Rev. 84, 844 (1951).

[15]J. H. Burkhalter, R. S. Anderson, W. V. Smith, and W. Gordy, Phys. Rev. 79, 651 (1950).

[16]L. F. Stafford, and C. W. Tolbert, J. Geophys. Res. 68, 3431 (1963).

PHYSICAL REVIEW A VOLUME 5, NUMBER 2 FEBRUARY 1972

Convergence of the $1/Z$ Expansion*

Reinhart Ahlrichs†
Laboratory of Molecular Structure and Spectra, Department of Physics, University of Chicago, Chicago, Illinois 60637
(Received 9 June 1971)

Lower bounds to the convergence radii of the $1/Z$ expansions are reported for some low-lying states of the isoelectronic series of the helium and lithium atom. It is proven for the first time that the $1/Z$ expansion converges for the ground state of the helium atom. The investigation of the $1\,^2S$ and $1\,^2P_u$ states of the lithium atom indicated poor convergence properties of the $1/Z$ expansion for systems with more than two electrons. The Brillouin-Wigner perturbation expansion of the ground state of the helium atom is shown to converge if $1/(Z - \sigma)$ is used as perturbation parameter for $\sigma = 0.34$.

I. INTRODUCTION

Different kinds of perturbation theoretical approaches have been used extensively in the quantum-mechanical treatment of electronic wave functions and energies of small atoms. Since the perturbation equations cannot be solved explicitly in this case, one has to use approximate methods of evaluation, e.g., variational techniques. Most commonly used is the Hylleraas-Knight-Scheer (HKS) variational perturbation method[1,2] which has been successfully applied to treat the Rayleigh-Schrödinger perturbation expansion (RSPE)[3–5] and the Brillouin-Wigner perturbation expansion (BWPE)[6] of several electronic states of first-row atoms.

In connection with the use of the HKS method or a related technique we meet two problems of principal interest. (a) Since the variational perturbation procedure yields only an approximation to the nth-order wave function and energy, it is important to establish error bounds for these quantities. (b) A rigorous justification for the use of perturbation theory itself must be given, i.e., to prove the convergence of the usually unknown exact perturbation

expansion for the wave function and energy under consideration.

The first problem has been the subject of numerous investigations,[7] but no generally applicable method seems to have been proposed that allows one to calculate error bounds for both the individual nth-order contributions to the wave function and the energy. An investigation of this problem will be published elsewhere.[8] In this paper we will be mainly concerned with the second problem. In Sec. II we first give a very short account of the basic mathematical concepts and develop some formulas to facilitate the subsequent applications. Of special importance is the investigation of the "screening approach" (Secs. II C and II D) which leads to considerably improved lower bounds of the convergence radius of the $1/Z$ expansion. In Sec. II E we discuss briefly the relationship between the convergence properties of the exact RSPE and the "approximate RSPE" as furnished by the HKS method. The theory outlined in Sec. II is applied in Sec. III to calculate lower bounds for the exact-convergence radii of the $1/Z$ RSPE for some low-lying states of the helium series. The $1\,^2S$ and $1\,^2P_u$ states of the lithium series are treated as a simple but representative example of a system with more than two electrons. The convergence of the BWPE is discussed briefly for the ground state of the helium series.

II. THEORY

A. Mathematical Background

In this section we repeat briefly some well-known facts in order to prepare for subsequent considerations. The starting point of our investigation is the eigenvalue equation of an atomic system (in atomic units)

$$H_Z \psi_Z = E_Z \psi_Z , \qquad \|\psi_Z\| = 1 \tag{1}$$

$$H_Z = T - Z\,U + V, \qquad T = -\sum_i \tfrac{1}{2}\Delta_i ,$$
$$U = \sum_i 1/r_i , \qquad V = \sum_{i<j} 1/r_{ij} , \tag{2}$$

where Z is the nuclear charge. For brevity we drop the index which labels the different solutions of (1).

At first we note that H_Z is invariant under the rotation reflection group O_{3i} and under the group of all permutations of the electrons. Although we will take advantage of these symmetry properties (see Secs. III D and III E), we will not discuss these matters in detail and refer the reader to the literature.[9–11] We only note that the invariance of H_Z under symmetry operations allows H_Z to be decomposed into the direct sum of several parts acting in mutually orthogonal subspaces [of the total Hilbert space $\underline{H} = \underline{L}^2(R^{3n})$] characterized by various symmetry properties. We will thus have to consider only that part of H_Z which is determined by the symmetry of the state under consideration. Although the total wave function depends on the space *and* spin variables of the electrons, it is sufficient to consider the eigenvalue equation (1) in the Hilbert space $\underline{H} = \underline{L}^2(R^{3n})$ of spin-independent functions, since there is a one to one relationship between the total spin and the behavior of ψ_Z under particle permutations.[11]

We return to the discussion of Eqs. (1) and (2). Replacing the variables $\vec{r}_i$ by the scaled variables $(Z\vec{r}_i)$ yields the new eigenvalue equation

$$H_\lambda \psi_\lambda = E_\lambda \psi_\lambda , \tag{3}$$

with the Hamiltonian

$$H_\lambda = H_0 + \lambda V , \quad H_0 = T - U \tag{4}$$

where $\lambda = 1/Z$.

The eigenvalues and eigenfunctions of (1) and (3) are related through

$$E_Z = Z^2 E_\lambda , \quad \psi_Z(\vec{r}_1, \ldots, \vec{r}_n) = Z^{3n/2} \psi_\lambda(Z\vec{r}_1, \ldots, Z\vec{r}_n) \tag{5}$$

Equations (3) and (4) are a common starting point for the use of perturbation theory. In the RSPE the wave function ψ_λ and energy E_λ are expanded in power series in λ:

$$\psi_\lambda = \sum_\nu \lambda^\nu \psi_{(\nu)} , \quad E_\lambda = \sum_\nu \lambda^\nu E_{(\nu)} . \tag{6}$$

Both $E_{(\nu)}$ and $\psi_{(\nu)}$, the latter up to a common phase factor, are uniquely determined by the ansatz (6) and the eigenvalue equation (3). Kato[12] has shown that H_λ, defined in (4), forms a self-adjoint holomorphic family of type A for all complex λ. This assures that the series expansions (6) converge for sufficiently small λ, provided E_0 is an isolated eigenvalue of H_0 with finite multiplicity.[12] Since H_0 is bounded from below, H_λ is also a holomorphic self-adjoint family of type B.[13]

B. Lower Bounds to Convergence Radius

Let E_0 be an isolated nondegenerate eigenvalue of H_0 and E_0^+, E_0^- ($E_0^- < E_0 < E_0^+$) be the neighboring points of the spectrum of H_0. Let a and b ($b \geq 0$) be real constants, such that

$$|(Vf, f)| \leq a(f,f) + b(H_0 f, f) , \quad f \in \underline{D}(H_0) \tag{7}$$

where $\underline{D}(H_0)$ denotes the domain of H_0. The RSPE (6) is then convergent, at least if $|\lambda| < r_1$, with r_1 given by

$$r_1 = \min(r_+, r_-) , \quad r_\pm = \frac{|E_0 - E_0^\pm|}{2a + b(E_0 + E_0^\pm)} . \tag{8}$$

For the derivation of (8), which is essentially based on the results of Kato,[12] the reader is referred to Ref. 14.

In order to facilitate subsequent applications we will now rewrite (7) and (8). Since H_λ is a holomorphic family of type B for all complex λ, the operators $H_0 + yV$ and $H_0 - yV$ are bounded from below for all real $y \geq 0$.[13] (It is convenient not to use the perturbation parameter λ in this context, but to introduce a new real positive parameter y.)

Let $C_+(y)$ and $C_-(y)$ be two functions, such that (9a) and (9b) are fulfilled for $y \geq 0$,

$$H_0 + yV \geq -C_+(y) , \tag{9a}$$

$$H_0 - yV \geq -C_-(y) . \tag{9b}$$

[For a Hermitian operator T, we write $T \geq C$ if

$$(Tf, f) \geq C(f, f) , \quad f \in \underline{D}(T) .$$

It should be noted that $\underline{D}(H_\lambda) = \underline{D}(H_0)$, since H_λ is also a holomorphic family of type A (Sec. VII 2 of Ref. 13).] Defining

$$C(y) = \max(C_+(y) , C_-(y)) , \tag{10}$$

the inequalities (9a) and (9b) can be combined to give

$$|(Vf, f)| \leq (C(y)/y)\,(f,f) + (1/y)\,(H_0 f, f) .$$

This is a relationship of the form (7) with $a = C(y)/y$ and $b = 1/y$. Inserting this into (8) we obtain

$$r_1 = \min(r_+, r_-) , \quad r_\pm = \frac{y\,|E_0 - E_0^\pm|}{2\,C(y) + E_0 + E_0^\pm} . \tag{11}$$

The expression for r_1 makes the relationship between the calculation of lower bounds (r_1) of the convergence radius and the calculation of lower bounds of $H_0 \pm yV$ more transparent. In order to make r_1 as large as possible, we will always optimize r_1 with respect to y. Equation (11) is a convenient starting point for this procedure.

The perturbation V defined in (2) is a positive operator $V \geq 0$. Consequently, we have $C_-(y) \geq C_+(y)$ and hence

$$C(y) = C_-(y) \tag{12}$$

in this case.

C. Screening Approach

In Sec. II B we used a scaling transformation with scaling parameter Z to bring the eigenvalue equation (1) to the form (3) which is suited for a treatment by perturbation theory. Fröman and Hall[15] and later Kato[16] have investigated a different approach where $(Z - \sigma)$ is used as scaling parameter. The so-called screening constant σ can in principle be any real number with $Z - \sigma > 0$; otherwise the scaling transformation is unreasonable. It turns out, however, that we have to discuss only positive screening constants, $\sigma > 0$.

We now obtain the new eigenvalue equation[15]

$$H_\mu^\sigma \psi_\mu^\sigma = E_\mu^\sigma \psi_\mu^\sigma , \tag{13}$$

$$H_\mu^\sigma = H_0 + \mu\, W^\sigma , \quad W^\sigma = V - \sigma U , \tag{14}$$

$$\mu = 1/(Z - \sigma) , \tag{15}$$

where the superscript σ indicates the explicit dependence of the solutions E_μ^σ and ψ_μ^σ of (13) on the parameter σ.

Next, we prove a relationship between the lower bound r_1^σ for the convergence radius of the RSPE of E_μ^σ and ψ_μ^σ in μ and the lower bound r_1 for the λ expansion (6),

$$r_1^\sigma \geq 2\, r_1 , \tag{16}$$

provided the following conditions are met.

(a) $C_-(y)$ [see (9b)] is of the form

$$C_-(y) = -E_{0,0}(1 + \eta y)^2 , \quad \eta > 0 \tag{17}$$

where $E_{0,0}$ denotes the lowest eigenvalue of H_0.

(b) Then, we require

$$1 - y\sigma > 0 \tag{18}$$

for all values of y and σ of interest, i. e., for those values of y and σ for which r_1^σ assumes a maximum.

(c) σ is chosen in a particular way, namely, according to (25).

We note that (17) and (18) are fulfilled in all applications treated in Sec. III of this study.

While V was a positive operator, W is indefinite and we have to consider both cases in (9). Performing appropriate scalings one easily obtains

$$H_0 + yW \rightarrow (1 + y\sigma)^2 \{H_0 + [y/(1 + y\sigma)]\, V\} \geq -C_+^\sigma(y) , \tag{19a}$$

$$H_0 - yW \rightarrow (1 - y\sigma)^2 \{H_0 + [y/(1 - y\sigma)]\, V\} \geq -C_-^\sigma(y) , \tag{19b}$$

where we have used (18) in order to obtain (19b). Relationships (19) relate the bounds $C_\pm^\sigma(y)$ to the bounds $C_\pm(y)$ defined in (9):

$$C_+^0(y) = (1 + y\sigma)^2\, C_+[y/(1 + y\sigma)] , \tag{20a}$$

$$C_-^0(y) = (1 - y\sigma)^2\, C_-[y/(1 - y\sigma)] . \tag{20b}$$

Combining (20b) and (17) yields

$$C_-^\sigma(y) = -E_{0,0}\,(1 - y\sigma + \eta y)^2 . \tag{21}$$

As V is positive a lower bound $C_+(y)$ is given by

$$C_+(y) = -E_{0,0} , \tag{22}$$

which gives

$$C_+^\sigma(y) = -E_{0,0}(1 + y\sigma)^2 . \tag{23}$$

Next, we will determine σ in order to make r_1^σ as large as possible. In analogy to (11), r_1^σ is given by

$$r_1^\sigma = \min(r_+^\sigma, r_-^\sigma) , \quad r_\pm^\sigma = \frac{y\,|E_0 - E_0^\pm|}{2\,C^\sigma(y) + E_0 + E_0^\pm} , \tag{24}$$

with $C^\sigma(y) = \max(C_+^\sigma(y),\ C_-^\sigma(y))$.

It is now an easy matter to verify that r_1^σ assumes a maximum for

$$\sigma = \tfrac{1}{2}\eta \tag{25}$$

independent of the actual values of all other quantities entering (24). From (25), (21), and (23) one obtains immediately

$$C^\sigma(y) = C_+^\sigma(y) = C_-^\sigma(y) = -E_{0,0}(1+\tfrac{1}{2}\eta y)^2 . \tag{26}$$

Inserting (26) into (24) yields, by comparison with (11),

$$r_\pm^\sigma(y) = 2\, r_\pm(\tfrac{1}{2}y) , \tag{27}$$

which proves (16). In the unscreened expansion (4) and in the screened expansion (14), we are dealing with the same unperturbed operator H_0, hence E_0, E_0^+, E_0^- have the same values in each case. The "greater than" sign in (16) appears because we used the rather crude estimate (22) for $C_+(y)$. If a better lower bound to $H_0 + yV$ than (22) is available one will, of course, obtain a larger value for r_1^σ than $2r_1$.

D. Relationship between Screened and Unscreened Perturbation Expansions

Starting from the definition (14) of H_μ^σ we perform a scaling transformation with the scaling parameter $\mu/(1+\sigma\mu)$, which is reasonable for real positive μ, and obtain

$$H_\mu^\sigma \rightarrow (1+\sigma\mu)^2\{H_0 + [\mu/(1+\sigma\mu)]\, V\} . \tag{28}$$

From (28) we deduce immediately

$$E_{\mu/(1+\sigma\mu)} = [1/(1+\sigma\mu)^2]\, E_\mu^\sigma . \tag{29}$$

Setting

$$\lambda = \mu/(1+\sigma\mu) \rightarrow \mu = \lambda/(1-\sigma\lambda) \tag{30}$$

we can rewrite (29) as

$$E_\lambda = (1-\sigma\lambda)^2\, E^\sigma_{\lambda/(1-\sigma\lambda)} . \tag{31}$$

Now both E_λ and E_μ^σ are analytical functions for sufficiently small λ and μ, and hence (29) and (31) are not only valid for $\mu > 0$ but also for complex values of μ (principle of analytic continuation; see, e.g., Ref. 17).

Since E_μ^σ is an analytical function, at least for $|\mu| < r_1^\sigma$, we have thus proven the regularity of E_λ for all λ fulfilling

$$|\lambda/(1-\sigma\lambda)| < r_1^\sigma . \tag{32}$$

In the complex λ plane the set defined by (32) forms the interior of a circle with radius

$$R = \frac{r_1^\sigma}{1-\sigma^2(r_1^\sigma)^2}$$

centered at

$$M = -\frac{\sigma(r_1^\sigma)^2}{1-\sigma^2(r_1^\sigma)^2} .$$

The largest circle centered at the origin contained in the set defined by (32) has the radius $\tilde{r}$:

$$\tilde{r} = \frac{r_1^\sigma}{1+\sigma r_1^\sigma} . \tag{33}$$

Stated differently, we have proven the convergence of the expansion (6) of E_λ for

$$|\lambda| < \tilde{r} . \tag{34a}$$

Using $r_1^\sigma \geq 2\, r_1$ [see (16)], (34a) implies the convergence of the $1/Z$ expansion for

$$Z > Z_0 = 1/2r_1 + \sigma . \tag{34b}$$

It is now an easy matter to see that even the RSPE for ψ_λ [Eq. (6)] has no singularities for the subset of the complex plane defined by (32). From the way the lower bound for the convergence radius is obtained in the treatment of Kato[12] it follows immediately that the eigenvalue E_μ^σ of H_μ^σ does not cross any other eigenvalue of H_μ^σ for $|\mu| < r_1^\sigma$. Since the relationship (31) holds for all eigenvalues of H_μ^σ and H_λ, we conclude that E_λ does not cross any other eigenvalue of H_λ if (32) is fulfilled. This finally proves the regularity of ψ_λ, since ψ_λ can have a singularity only if the corresponding eigenvalue E_λ crosses some other eigenvalue of H_λ (Secs. II 1 and VII 1 of Ref. 13).

These somewhat difficult considerations were necessary because the scaling parameter $\mu/(1+\sigma\mu)$, which was used to establish the relationship between H_μ^σ and H_λ and consequently ψ_μ^σ and ψ_λ, depends on the perturbation parameter used. This makes it almost impossible to compare the perturbation expansions of ψ_μ^σ and ψ_λ directly.

Expansion (6) must in fact have a larger convergence radius than $\tilde{r}$ given in (33). The circles enclosing the sets of complex numbers defined in (32) and (34) have only the point $\lambda = \tilde{r}$ in common. As has been proven by Rellich,[18] no singularity of E_λ or ψ_λ can occur for real values of the perturbation parameter, hence the RSPE [Eq. (6)] can be continued analytically beyond the circle $|\lambda| = \tilde{r}$.

E. Comments on HKS Method

In this subsection we discuss briefly some features of the variation perturbation technique in connection with convergence properties. Let us denote by $\tilde{\psi}_{(\nu)}$ and $\tilde{E}_{(\nu)}$ the approximations for the corresponding exact terms furnished by a HKS calculation. In theoretical investigations and practical applications the $\tilde{\psi}_{(\nu)}$ are almost exclusively written as linear combinations of the very same basis set χ_i, $i = 1, \ldots, m$ (see, e.g., the discussion in Ref. 4):

$$\tilde{\psi}_{(\nu)} = \textstyle\sum_i C_i^{(\nu)} \chi_i , \quad \nu = 0, 1, 2, \ldots . \tag{35}$$

The subsequent discussions are based on the following interpretation of the variational perturbation method. The coefficients $C_i^{(\nu)}$ [see (35)] and perturbation energies $\tilde{E}_{(\nu)}$ furnished by a variational perturbation calculation are identical with the corresponding terms obtained from a perturbation expansion (37) of the secular equation (36), which results from the variational treatment of the eigenvalue problem (3) by using the same linear basis χ_i as in (35):

$$\sum_k (H_\lambda)_{ik} C_{\lambda,k} = \tilde{E}_\lambda C_{\lambda,i} , \tag{36}$$

$$\tilde{E}_\lambda = \sum_\nu \lambda^\nu \tilde{E}_{(\nu)} , \quad C_{\lambda,i} = \sum_\nu \lambda^\nu C_i^{(\nu)} , \tag{37}$$

$$(H_\lambda)_{ik} = \langle \chi_i | H_0 | \chi_k \rangle + \lambda \langle \chi_i | V | \chi_k \rangle . \tag{38}$$

Stated differently: The term "variational perturbation method" is as suited to describe the HKS procedure as is the term "perturbational variation method," provided one starts from (35).

This relationship, which is more or less obvious from the HSK equations, has been realized by some workers in this field.[19] Midtdal[3] has even given a rather elaborate proof, but has never discussed this aspect, which he calls a formal identity.

We will now draw a few conclusions from this interpretation of the variational perturbation method.

(a) If $H_0 \pm y V (y \geq 0)$ is bounded from below by $-C_\pm(y)$ [see Eq. (9)], then, by virtue of the variational principle, we have also $\tilde{H}_0 \pm y \tilde{V} \geq -C_\pm(y)$, where $\tilde{H}_0$ and $\tilde{V}$ denote the finite-dimensional matrices with matrix elements defined in (38). Let us assume that the unperturbed operator H_0 and the unperturbed matrix $\tilde{H}_0$ have the eigenvalues E_0, E_0^+, and E_0^- in common. Under this condition the lower bound r_1 [Eq. (11)] to the exact convergence radius of the RSPE is also a lower bound to the convergence radius of the expansions (37), since $C_\pm(y)$ and E_0, E_0^+, E_0^- are the only quantities entering in the formula for r_1.

The same argument is of course applicable for a HKS treatment of the screened expansion discussed in II C. The relationship between the screened and unscreened expansion (see II D) does not hold in a variation perturbation treatment. The reason is as follows. In order to prove relationship (28) we had to perform a scaling transformation where the scaling parameter was a function of the perturbation parameter itself. Subjecting the basis functions χ_i to a scaling transformation is now quite a different matter, depending on whether the χ_i form a complete or an incomplete basis set. In the first case one has just a transformation to another complete basis and is dealing with different matrix representations of the very same operators H_0 and V. This is of course not the case if only a finite-dimensional basis is scaled and relations (28) and (31) do not hold.

(b) All eigenvalues of (36) are branches of one algebraic function (Sec. II 1 of Ref. 13). The exact convergence radius of the expansion (37) of $\tilde{E}_\lambda$ is consequently determined by the branch point nearest to $\lambda = 0$ in which the $\tilde{E}_\lambda$ under consideration is involved. The position of such a branch point depends strongly, in general, on the basis set χ_i and the number m of basis functions used in the calculation. Midtdal[3] has stated "that the perturbational convergence of the series expansions furnished by a HKS treatment is an inherent property of the atomic state, independent of the type of trial functions used." This statement is clearly correct as far as the convergence of the exact expansions is concerned. The perturbational convergence of the series expansions involving the $\tilde{E}_{(\nu)}$ and $\tilde{\psi}_{(\nu)}$ does, however, depend on the basis set. The very fact that $\tilde{E}_\lambda$ has only algebraic singularities determines more or less the behavior of the $\tilde{E}_{(\nu)}$ for large ν. This consequently depends strongly on the basis set χ_i, and especially on the number of basis functions used.

An investigation of the $\tilde{E}_{(\nu)}$ can at best provide information about the singularity of $\tilde{E}_\lambda$. Two such investigations of the $\tilde{E}_{(\nu)}$ obtained by Midtdal[3] for the ground state of the helium series have been reported[20,21]; both indicate that $\tilde{E}_\lambda$ has a singularity on the real axis close to $\lambda = 1.1$. This result is in contradiction with the well-known fact that $\tilde{E}_\lambda$, as an eigenvalue of $\tilde{H}_\lambda$, has no singularities on the real axis.[22]

III. RESULTS

In order to apply the theory explained in Sec. II, we simply have to derive a lower bound $C_-(y)$ for $H_0 - yV$ [see Eqs. (9) and (12)] and to evaluate (11) to obtain r_1. According to (34b) the convergence of the $1/Z$ expansion is then assured for

$$Z > Z_0 = (1/2r_1) + \sigma .$$

For the ^1S states the derivation of a lower bound $C_-(y)$ will be based solely on the relationship

$$-\tfrac{1}{2}\mu\Delta - \nu/|\vec{r} + \vec{s}| \geq -\nu^2/2\mu , \quad \nu \geq 0 , \quad \mu > 0 \tag{39}$$

where $\vec{s}$ can be any vector. To verify (39) we note that the lowest eigenvalue of the Hamiltonian operator of the hydrogen atom $h = -\tfrac{1}{2}\Delta - 1/(|\vec{r} + \vec{s}|)$ (nucleus at $-\vec{s}$) is $-\tfrac{1}{2}$, hence h is bounded from below with the bound $-\tfrac{1}{2}(h \geq -\tfrac{1}{2})$. Performing an appropriate scaling transformation one easily derives (39).

For the treatment of the states of symmetry ^3S, ^1P_u, ^3P_u, and ^3P_g we will also use

$$[-\tfrac{1}{2}\mu\Delta - \nu/r]^u \geq -\nu^2/8\mu , \tag{40}$$

where the superscript u denotes the ungerade part of the operator, i.e., the operator acting only in the space of odd functions. Relationship (40) is

proven in analogy to (39), since the $2p$ state with eigenvalue $-\frac{1}{8}$ is the lowest-lying state of $h=-\frac{1}{2}\Delta - 1/r$ with ungerade symmetry.

A. $1\,^1S$ and $2\,^1S$ States of Helium Series

The singlet states of a two-electron system are associated with symmetric solutions $\psi_\lambda(\vec{r}_1, \vec{r}_2) = \psi_\lambda(\vec{r}_2, \vec{r}_1)$ of the eigenvalue equation (3). In this case, however, the symmetry behavior is of no importance for the following treatment. Introducing the variables

$$\vec{R}=\tfrac{1}{2}(\vec{r}_1+\vec{r}_2), \quad \vec{r}_{12}=\vec{r}_1-\vec{r}_2 , \tag{41}$$

we obtain in an obvious notation

$$-\tfrac{1}{2}\Delta_1-\tfrac{1}{2}\Delta_2=-\Delta_{12}-\tfrac{1}{4}\Delta_R . \tag{42}$$

$H_0 - yV$ can then be juggled to give

$$\begin{aligned} H_0-yV &= -\sum_{i=1,2}\left(\frac{\Delta_i}{2}+\frac{1}{r_i}\right)-\frac{y}{r_{12}} \\ &= -\sum_i\left((1-\alpha)\frac{\Delta_i}{2}+\frac{1-\gamma}{r_i}\right) \\ &\quad -\alpha\Delta_{12}-\frac{y}{r_{12}}-\sum_i\left(\alpha\frac{\Delta_R}{8}+\frac{\gamma}{r_i}\right), \end{aligned} \tag{43}$$

where α and γ are real numbers satisfying

$$0<\alpha<1, \quad 0\le\gamma\le 1 . \tag{44}$$

Inserting

$$\vec{r}_1=\vec{R}+\tfrac{1}{2}\vec{r}_{12}, \quad \vec{r}_2=\vec{R}-\tfrac{1}{2}\vec{r}_{12}$$

in the last term on the right-hand side of (43) and applying (39) straightforwardly, one finds that

$$H_0-yV\ge-\frac{(1-\gamma)^2}{1-\alpha}-\frac{y^2}{4\alpha}-\frac{4\gamma^2}{\alpha} . \tag{45}$$

In order to make the right-hand side of (45) as large as possible we optimize α and γ under restrictions (44) and obtain

$$C_-(y)=\begin{cases}(1+\frac{1}{4}\sqrt{3}\,y)^2 & \text{if } 0\le y\le 4\sqrt{3}\\ 4+\frac{1}{4}y^2 & \text{if } y\ge 4\sqrt{3}\end{cases} . \tag{46}$$

Since $E_{0,0}=-1$, $C_-(y)$ is of the form (20), provided $y\le 4\sqrt{3}$, which will always be the case in the following. Estimate (46) is slightly better than the result of Kato,[12] who obtained $C_-(y)=(1+\frac{1}{2}y)^2$. From the treatment of Stillinger[20] it follows that $C_-(y)$ as given in (46) approaches the exact lowest eigenvalue of H_0-yV for large y up to a term proportional to y^{-2}.

$1\,^1S$ State

Inserting $E_0=-1$, $E_0^-=-\infty$, $E_0^+=-\frac{5}{8}$ together with (46) into (11) yields, after optimization with respect to y,

$$r_1=\frac{3}{6+8\sqrt{3}}\approx\frac{1}{6.6} , \tag{47}$$

where the optimal y is $y_0=1$. Comparing (46) with (17) we obtain the optimal screening constant σ in accordance with (25) as

$$\sigma=\tfrac{1}{8}\sqrt{3} .$$

By virtue of (34b) we have thus proven the convergence of the $1/Z$ expansion of the ground state of the isoelectronic series of the helium atom for

$$Z>Z_0=\tfrac{1}{3}(3+4\sqrt{3})+\tfrac{1}{8}\sqrt{3}\approx 3.5 . \tag{48}$$

$2\,^1S$ State

In this case one has $E_0=-\frac{5}{8}$, $E_0^-=-1$, $E_0^+=-\frac{5}{72}$, which yields

$$r_1=\frac{5}{(27)^{1/2}}\,\frac{1}{2(131)^{1/2}+24}\approx\frac{1}{48.7}$$

for

$$y_0=\left(\frac{131}{27}\right)^{1/2} , \tag{49}$$

$$Z_0\approx 24.6 . \tag{50}$$

B. Refined Treatment of $1\,^1S$ State of Helium Series

We now go beyond the rather crude estimate (22) and use a calculation by Bazley[23] to obtain a better lower bound to H_0+yV. Using again $C_-(y)$ as given in (46) and the Bazley bound $C_+(y)$ as described in the Appendix, the formula [Eq. (24)] for r_1^σ was then evaluated numerically. The largest value for r_1^σ was obtained for the σ and y values close to

$$\sigma=0.34, \quad y=1.75 . \tag{51}$$

Inserting these values yields

$$r_1^\sigma=0.608 . \tag{52}$$

By virtue of (33) and (34) this assures the convergence of the $1/Z$ expansion for

$$Z>Z_0=1.98 . \tag{53}$$

C. Convergence of BWPE for $1\,^1S$ State

Starting from relationship (7), the convergence of the BWPE can be proven if

$$y^{-1}|\lambda|\,\|[C(y)+H_0]S_0(E_\lambda)\|<1 \tag{54}$$

holds for some y.[24] Here $S_0(E_\lambda)$ denotes the reduced resolvent of H_0 with respect to the unperturbed eigenvalue E_0 of H_0 [see Eqs. (14), (47a), and (48) of Ref. 24, to which the reader is referred for all details]. The parameters a and b in Ref. 24 are in the present treatment given by $C(y)(1/y)=a$ and $1/y=b$ (see Sec. II B). We further note that E_λ in (54) can be replaced by an upper bound to E_λ if the ground state is considered.[25] Using Kato's lower bound

$$H_0 - yV \geq -(1+\tfrac{1}{2}y)^2 , \tag{55}$$

we prove the convergence of the $1/Z$ BWPE for[24] $Z > 5.9$.

Replacing (55) by the slightly better expression (46), one obtains in just the same way the convergence for

$$Z > 5.4 . \tag{56}$$

From numerical evidence,[6] it has been concluded that the BWPE converges for $Z \gtrsim 3$, hence (56) is not too far off.

Concerning the $1/(Z-\sigma)$ expansion [see Eqs. (13)–(15)], the convergence of the BWPE can be proven for $Z=2$ (see below), but not for $Z=1$. In the case $Z=2$, i.e., the helium atom, a trivial numerical investigation shows that the left-hand side of (54) assumes a minimum close to the σ and y values given in (51). Inserting these numbers together with $\mu = (2-\sigma)^{-1}$ and $E_\mu^\sigma \geq -\mu^2\, 2.90372$ yields

$$y^{-1}\mu \,\|[C^\sigma(y) + H_0]S_0(E_\mu^\sigma)\| \leq 0.584 . \tag{57}$$

[According to (7) and (31) the upper bound -2.90372 (Ref. 26) for the $1\,^1S$ state of helium has to be "screened" by μ^2.] The result [Eq. (57)] can more or less be interpreted in the following way: The BWPE for the energy and wave function are, in the case under consideration, majorized by a geometric series with $q = 0.584$, indicating quite comfortable convergence properties.

For the BWPE there seems to be no relationship between the screened and unscreened expansion as was discussed in Sec. II D for the RSPE.

D. Lowest-Lying States of Symmetries ^3S, ^1P_u, ^3P_u, and ^3P_g of Helium Series

In this subsection the RSPE is discussed for some interesting low-lying excited states which are, however, ground states of the corresponding parts of the total Hamiltonian (see the discussion in Sec. II A).

Let us first note that we could of course use the bound $C_-(y)$ given in (46) in order to calculate r_1 and Z_0 values for any state of any symmetry, since we did not use symmetry properties at all to derive (46). Proceeding this way we would obtain exactly the same r_1 and Z_0 values as reported for the $2\,^1S$ state [see Eqs. (49) and (50)] for the states $1\,^3S$, $1\,^1P_u$, and $1\,^3P_u$. In order to improve these results, one has to exploit symmetry properties, which is a trivial matter for two-electron systems.

The lowest-lying states of H_0 of the corresponding symmetries arise from the following configurations:

$$1\,^3S , \qquad 1s\,2s , \qquad E_0 = -\tfrac{5}{8} ;$$

$$1\,^1P_u ,\ 1\,^3P_u , \qquad 1s\,2p , \qquad E_0 = -\tfrac{5}{8} ;$$

$$1\,^3P_g , \qquad 2p^2 , \qquad E_0 = -\tfrac{1}{4} .$$

Thus, in analogy to (39) we have

$$-\sum_{i=1,2}\left(\mu\frac{\Delta_i}{2} + \frac{\nu}{r_i}\right) \geq \begin{cases} -\frac{5}{8}(\nu^2/\mu) & \text{for } {}^3S,\ {}^1P_u, \text{ and } {}^3P_u \\ -\frac{1}{4}(\nu^2/\mu) & \text{for } {}^3P_g . \end{cases} \tag{58}$$

Next, we note that triplet states are associated with antisymmetric wave functions $\psi(\vec{r}_1, \vec{r}_2) = -\psi(\vec{r}_2, \vec{r}_1)$ or equivalently $\psi(\vec{R}, \vec{r}_{12}) = -\psi(\vec{R}, -\vec{r}_{12})$. Consequently, (59) holds [see (40)] for triplet states:

$$-\tfrac{1}{2}\mu\,\Delta_{12} - \nu/r_{12} \geq -\nu^2/8\mu . \tag{59}$$

Starting again from expression (43) we thus obtain, using (58) and (59),

$$H_0 - yV \geq \begin{cases} -\frac{5}{8}\frac{(1-\gamma)^2}{1-\alpha} - \frac{y^2}{4\alpha} - \frac{4\gamma^2}{\alpha} , & {}^1P_u \\ -\frac{5}{8}\frac{(1-\gamma)^2}{1-\alpha} - \frac{y^2}{16\alpha} - \frac{4\gamma^2}{\alpha} , & {}^3S \text{ and } {}^3P_u \\ -\frac{1}{4}\frac{(1-\gamma)^2}{1-\alpha} - \frac{y^2}{16\alpha} - \frac{4\gamma^2}{\alpha} , & {}^3P_g . \end{cases} \tag{60}$$

Optimizing these lower bounds with respect to α and γ under restrictions (44) yields the following $C_-(y)$:

$$C_-(y) = \begin{cases} \frac{5}{8}(1+\frac{3}{4}(\frac{3}{5})^{1/2}y)^2 , & 0 \leq y \leq 12(\frac{3}{5})^{1/2} \\ 4 + \frac{1}{4}y^2 , & y \geq 12(\frac{3}{5})^{1/2} \end{cases} \quad \text{for } {}^1P_u , \tag{61a}$$

$$C_-(y) = \begin{cases} \frac{5}{8}(1+\frac{3}{8}(\frac{3}{5})^{1/2}y)^2 , & 0 \leq y \leq 24(\frac{3}{5})^{1/2} \\ 4 + \frac{1}{16}y^2 , & y \geq 24(\frac{3}{5})^{1/2} \end{cases} \quad \text{for } {}^3S,\ {}^3P_u \tag{61b}$$

$$C_-(y) = \begin{cases} \frac{1}{4}[1+\frac{1}{8}(15)^{1/2}y]^2 , & 0 \leq y \leq 8(15)^{1/2} \\ 4 + \frac{1}{16}y^2 , & y \geq 8(15)^{1/2} \end{cases} \quad \text{for } {}^3P_g \tag{61c}$$

The evaluation of (11) is straightforward and the results are summarized in Table I, where we have included the treatment of the $1\,^1S$ and $2\,^1S$ states (see Sec. III A) for completeness.

E. ^2S Ground State of Lithium Series

The doublet states of a system of three spin-$\frac{1}{2}$ particles are associated with the only two-dimensional irreducible representation of S_3. We choose the two spin functions spanning this representation as

$$\begin{aligned} \theta_1 &= (1/\sqrt{2})\,(\alpha\beta\alpha - \beta\alpha\alpha) , \\ \theta_2 &= (1/\sqrt{6})\,(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha) . \end{aligned} \tag{62}$$

Any doublet function $\psi(\vec{r}, \vec{s})$ ($\vec{r}$ and $\vec{s}$ denote the space and spin variables, respectively) can then be written as

$$\psi(\vec{r}, \vec{s}) = (1/\sqrt{2})\,[\phi_1(\vec{r})\,\theta_1 + \phi_2(\vec{r})\,\theta_2] . \tag{63}$$

The spatial functions ϕ_1 and ϕ_2 again span the two-

dimensional irreducible representation of S_3, which follows immediately from the antisymmetry of $\psi(\vec{r}, \vec{s})$. According to the discussion in Sec. II A it is now sufficient to consider only the part $H_\lambda^{(2)}$ of the total Hamiltonian H_λ, which acts in the space of functions behaving like ϕ_2 with respect to permutations of the coordinates $\vec{r}_1$, $\vec{r}_2$, $\vec{r}_3$. We especially note the following property of ϕ_2:

$$\phi_2(\vec{r}_1, \vec{r}_2, \vec{r}_3) = -\phi_2(\vec{r}_2, \vec{r}_1, \vec{r}_3) , \tag{64}$$

which follows immediately from the antisymmetry of ψ.

The lowest eigenvalue of $H_0^{(2)}$ arises from the configuration $1s^2 2s$, $E_0 = -\frac{9}{8}$, and has multiplicity one. The first excited state is due to $1s^2 3s$, $E_0^+ = -\frac{19}{18}$. In order to derive a lower bound $C_-(y)$ for $H_0^{(2)} + yV^{(2)}$ we introduce the variables

$$\begin{aligned} &\vec{r}_{ij} = \vec{r}_i - \vec{r}_j , \quad i<j \\ &\vec{R} = \tfrac{1}{3}(\vec{r}_1 + \vec{r}_2 + \vec{r}_3) . \end{aligned} \tag{65}$$

If Δ_{ij} $(i<j)$ and Δ_R denote the Laplacians with respect to $\vec{r}_{ij}$ and $\vec{R}$, the following equality holds:

$$-\tfrac{1}{2} \sum_{i=1,3} \Delta_i = -\tfrac{2}{3} \sum_{i<j} \Delta_{ij} - \tfrac{1}{6} \Delta_R . \tag{66}$$

In analogy with Eq. (43) we obtain

$$\begin{aligned} (H_0 - yV)^{(2)} &= \left[-\sum_{i=1,3} \left(\frac{\Delta_i}{2} + \frac{1}{r_i} \right) - y \sum_{i<j} \frac{1}{r_{ij}} \right]^{(2)} \\ &= \left[-\sum_{i=1,3} \left((1-\alpha)\ \frac{\Delta_i}{2} + \frac{1-\gamma}{r_i} \right) \right. \\ &\quad \left. - \sum_{i<j} \left(2\alpha\ \frac{\Delta_{ij}}{3} + \frac{y}{r_{ij}} \right) - \sum_{i=1,3} \left(\alpha\ \frac{\Delta_R}{18} + \frac{\gamma}{r_i} \right) \right]^{(2)} \\ &\geq -\frac{9}{8} \left(\frac{(1-\gamma)^2}{1-\alpha} + \frac{0.75\, y^2}{\alpha} + \frac{12\gamma^2}{\alpha} \right) , \end{aligned} \tag{67}$$

where the $\geq$ sign holds only in the subspace of functions behaving like ϕ_2.

To derive the right-hand side of (67) we have taken advantage of (64) which requires

$$-\tfrac{1}{2}\mu\Delta_{12} - \nu/r_{12} \geq -\nu^2/8\mu$$

[see also (40), (59)]. We have further inserted

$$-\tfrac{1}{2}\mu\Delta_R - \nu/r_1 \geq -\nu^2/2\mu .$$

Optimizing the right-hand side of (67) with respect to α $(0<\alpha<1)$ and γ $(0 \leq \gamma \leq 1)$ we finally obtain

$$C(y) = \begin{cases} \frac{9}{8}\left[1 + \frac{1}{4}(11)^{1/2} y\right]^2 , & 0 \leq y \leq 4(11)^{1/2} \\ \frac{9}{8}\left(12 + \frac{3}{4} y^2\right) , & y \geq 4(11)^{1/2} . \end{cases} \tag{68}$$

The evaluation of (11) for r_1 is straightforward and yields

TABLE I. Lower bounds for the convergence radii of the $1/Z$ expansion for the isoelectronic series of the helium atom.

State	1^1S	2^1S	1^3S, 1^3P_u	1^1P_u	1^3P_g
r_1^{-1}[a]	$1+8/(3)^{1/2} \approx 6.6$	$\frac{1}{8}(27)^{1/2}[2(131)^{1/2}+24] \approx 48.$	$(3.0375)^{1/2}(6+\sqrt{2}) \approx 12.6$	$(12.65)^{1/2}(6+\sqrt{2}) \approx 25.8$	$1.5\sqrt{3}+1.8(15)^{1/2} \approx 9.6$
Z_0[b]	3.5	24.6	6.6	13.2	5.0
σ_0[c]	$\frac{1}{8}\sqrt{3} \approx 0.22$	$\frac{1}{8}\sqrt{3} \approx 0.22$	$\frac{3}{16}\sqrt{0.6} \approx 0.15$	$\frac{3}{8}\sqrt{0.6} \approx 0.29$	$\frac{1}{16}(15)^{1/2} \approx 0.24$
y_0[d]	1	$\left(\frac{131}{27}\right)^{1/2}$	$\left(\frac{40}{243}\right)^{1/2}$	$\left(\frac{40}{243}\right)^{1/2}$	$4/(27)^{1/2}$

[a]See Eq. (11).
[b]See Eq. (34b).
[c]Optimum screening constant; see Eq. (25).
[d]y_0 denotes the optimum y value for which r_1 assumes a maximum.

TABLE II. Lower bounds to $H_0 + yV : H_0 + yV \geq -C_+(y)$.

y	1	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1
C_+	1.0	0.952 603	0.905 421	0.858 516	0.811 977	0.765 933	0.720 567	0.676 153	0.633 090	0.591 946	0.554 370	0.518 581

$$r_1 = \frac{5}{27}\,\frac{1}{(2.5)^{1/2}+3(11)^{1/2}} \approx \frac{1}{62.1}\,, \tag{69}$$

where the optimal value for y is

$$y_0 = \left(\frac{40}{991}\right)^{1/2}.$$

From the considerations concerning the relationship between the screening approach and the usual $1/Z$ expansion, we conclude that the $1/Z$ expansion converges for

$$Z > Z_0 = (1/2\,r_1) + \sigma_0 \approx 31.4\,.$$

The value for σ_0 is in accordance with (17), (25), and (68) calculated as

$$\sigma_0 = \tfrac{1}{8}\,(11)^{1/2} \approx 0.41\,.$$

The above considerations are also valid for the $1/Z$ expansion of the lowest lying ^2P state which arises from the configuration $1s\,^2 2p$.

IV. CONCLUSIONS

The investigations reported in this paper show the usefulness of Kato's procedure to calculate lower bounds to the exact convergence radius of the $1/Z$ expansion for low-lying states of the helium series. The results collected in Table I, which were obtained with little effort, establish the convergence of the $1/Z$ expansion for rather small values of Z for the ground states of symmetry ^1S, ^3S, ^1P_u, and ^3P_u. Investing somewhat more labor we proved the convergence of the $1/Z$ RSPE (see Sec. III B) and the $1/(Z-\sigma)$ BWPE (see Sec. III C) for the most interesting case of the ground state of the helium atom, i.e., for $Z=2$. This result indicates that the use of better lower bounds than the rather crude $C_+(y)$ [see (22)] will cut the Z_0 values in Table I by roughly a factor of 2.

These promising results should encourage further work along this line to give a rigorous justification of the use of high-order perturbation theory in the treatment of physically interesting problems.

It is quite interesting to look for a relationship between the Z_0 values (Table I) and the convergence properties displayed by the numerical results of Midtdal and co-workers.[3,4]

It is easily seen that both the variational and the perturbational convergence deteriorates in the order $1\,^1S$, $1\,^3P_g$, $1\,^3S$, $1\,^3P_u$, $1\,^1P_u$, $2\,^1S$, which is exactly the order of the Z_0 values collected in Table I. This relationship clearly shows the physical significance of the lower bounds r_1 to the exact-convergence radii obtained with Kato's method.

Having this in mind one should consider the large Z_0 values obtained for the $2\,^1S$ state of the helium series and the ground state of the lithium series as an indication of rather poor convergence properties of the $1/Z$ expansion for these states. This result is of course not unexpected. Switching on the interelectronic interaction reduces (in the case of the lithium atom) the effective nuclear charge experienced by the outer electron from 3 to about 1, which is a rather large effect.

ACKNOWLEDGMENT

The author is indebted to Professor C. C. J. Roothaan for the kind hospitality he enjoyed during his stay in Chicago.

APPENDIX: BAZLEY BOUND FOR $H_0 + yV$

Bazley[23] has proposed a method to obtain lower bounds to eigenvalues of operators of the form $H_0 + yV$, provided $V \geq 0$ and $y \geq 0$. The method was applied by Bazley to calculate a lower bound to the ground-state energy of the helium atom, i.e., the $y = 0.5$ case. Since the author listed all necessary matrix elements, it is a trivial matter to repeat his calculation for different y values (see Table II).

A lower bound $-C_+(y)$ for $H_0 + yV$ can then be obtained for general $y\,(y \geq 0)$ by linear interpolation. This is a strictly justified procedure since the lower bound to the lowest eigenvalue furnished by the Bazley procedure (as well as the true ground-state energy) always has a negative second derivative.

If the lower bound $-C_+(y)$ obtained this way exceeds $-\frac{17}{32}$ (the 3rd excited state of H_0 of ^1S symmetry) it has to be replaced by this value (see the discussion in Ref. 23).

---

*Work supported by the Advanced Research Projects Agency of the Department of Defense and monitored by U. S. Army Research Office—Durham, Durham, N. C. 27706 under Contract No. DAHC04 70 C 0037.

†Present address: Institut für Physikalische Chemie und Elektrochemie, Universität Karlsruhe, Karlsruhe, Germany.

[1]E. A. Hylleraas, Z. Physik 65, 209 (1930).

[2]R. E. Knight and C. W. Scherr, Phys. Rev. 128, 2675 (1962); J. Chem. Phys. 37, 2503 (1962); Rev. Mod. Phys. 35, 431 (1963).

[3]J. Midtdal, Phys. Math. Univ. Osloensis 32, (1966).

[4]K. Aashamar, G. Lyslo, and J. Midtdal, J. Chem. Phys. 52, 3324 (1970).

[5]R. E. Knight, Phys. Rev. 183, 45 (1969).

[6]E. Brändas and O. Goscinski, Phys. Rev. A 1, 552 (1969).

[7]For a survey the reader is referred to the review article by J. O. Hirschfelder, W. Byers Brown, and S. T. Epstein, in *Advances in Quantum Chemistry*, edited by P. D. Löwdin (Academic, New York, 1964), Vol. 1, p. 255.

[8]R. Ahirichs, Chem. Phys. Letters 10, 157 (1971).

[9]G. M. Zislin and A. G. Siglov, Izv. Akad. Nauk SSSR 29, 1261 (1965).

[10]T. Kato, Progr. Theoret. Phys. (Kyoto) 540, 3 (1961).

[11]F. A. Matsen, in Ref. 7.
[12]T. Kato, J. Faculty Sci. U. Tokyo 6, 145 (1951).
[13]T. Kato, *Perturbation Theory for Linear Operators* (Springer, Berlin, 1966), p. 403.
[14]W. A. Bingel and R. Ahlrichs, Intern. J. Quantum Chem. 3, 141 (1969).
[15]A. Fröman and G. G. Hall, J. Mol. Spectry. 7, 410 (1961). The lower bound r_1 for the convergence radius of the $1/(Z-\sigma)$ expansion of the ground state of the Helium series reported by Fröman and Hall is incorrect, because the authors did not take the absolute value of (Vf, f) in (7). This error was corrected by Kato (Ref. 16), who did not refer to the paper of Fröman and Hall, however.
[16]Reference 13, p. 412.
[17]K. Knopp, *Funktionentheorie* (Sammlung Göschen, Berlin, 1964), Vol. I.
[18]F. Rellich, Math. Ann. 113, 600 (1937).
[19]S. T. Epstein (private communication).
[20]F. H. Stillinger, J. Chem. Phys. 45, 3623 (1966).
[21]E. Brändas and O. Goscinski, Intern. J. Quantum Chem. 4, 571 (1970).
[22]Reference 13, p. 120.
[23]N. W. Bazley, Phys. Rev. 120, 144 (1960).
[24]R. Ahlrichs, Intern. J. Quantum Chem. 4, 149 (1970).
[25]Reference 24, p. 166.
[26]C. L. Pekeris, Phys. Rev. 112, 1649 (1958).

PHYSICAL REVIEW A VOLUME 5, NUMBER 2 FEBRUARY 1972

Radiative Transition Rates from the $2p3p\ ^3P$ and $2p3d\ ^{1,3}D$ States of the Helium Isoelectronic Sequence*

G. W. F. Drake
Department of Physics, University of Windsor, Windsor 11, *Ontario, Canada*
(Received 12 October 1971)

The Hylleraas-Scherr-Knight variation-perturbation method is applied to the calculation of oscillator strengths for the dominant transitions from the metastable $2p3p\ ^3P$ and $2p3d\ ^{1,3}D$ states of helium and the heliumlike ions. The results explain the absence of the $1s2p\ ^3P - 2p3p\ ^3P$ transition of He I from recent beam-foil excitation spectra.

I. INTRODUCTION

Many atoms possess rydberg series of doubly excited states which, although imbedded in the autoionizing continuum, are prevented from autoionizing by angular momentum and parity selection rules. Such states may be termed "metastable" since their lifetimes are determined by the relatively slow process of spontaneous emission of radiation, rather than autoionization. The $2p^2\ ^3P$ metastable state of helium is the most extensively studied.[1-3] A recent remeasurement of its energy[4] has corrected an earlier error and brought the theoretical and experimental energies into good agreement. Progress in the theoretical study of multiply excited states has been reviewed by Holøien.[5]

In previous papers,[2,6] we have applied the Hylleraas-Scherr-Knight $1/Z$ expansion perturbation technique to the calculation of the energies of the metastable $2p^2\ ^3P$, $2p3p\ ^1P$, $2p3p\ ^3P$, $2p3d\ ^1D$, and $2p3d\ ^3D$ states of the helium isoelectronic sequence. Direct variational bounds have also been obtained for the neutral helium eigenvalues as a check on the accuracy of the perturbation expansions. In this paper, we evaluate the oscillator strengths for those transitions from the $2p3p\ ^3P$, $2p3d\ ^3D$, and $2p3d\ ^1D$ states which are expected to be dominant. Results for the corresponding transitions from the $2p^2\ ^3P$ and $2p3p\ ^1P$ states have been reported previously.[2] Transitions involving the above states have been observed in beam-foil excitation spectra[7] and are of interest in the study of solar flares and the solar corona.[8,9]

The computational method is briefly summarized in Sec. II and the results presented in Sec. III.

II. COMPUTATIONAL METHOD

The Hylleraas-Scherr-Knight variation-perturbation method used in the present work has been described previously[2,6] and is only briefly summarized here. In units of Z^2 a.u., the Hamiltonian for a two-electron atom may be written in the form $H = H_0 + Z^{-1}V$, where H_0 is a sum of hydrogen-atom Hamiltonians and $V = 1/r_{12}$. The above partition of H leads to the following perturbation expansions for the eigenfunctions and eigenvalues:

$$\Psi = \Psi_0 + \sum_{n=1} \Psi_n Z^{-n}, \tag{1}$$

$$E = E_0 + \sum_{n=1} E_n Z^{-n}. \tag{2}$$

The perturbed functions Ψ_n are expressed in terms of a truncated set of N orthonormal functions φ_i, which are constructed from linear combinations of N correlated functions of the form