PHYSICAL REVIEW A VOLUME 5, NUMBER 4 APRIL 1972

Resonance Quasi-Projection Operators: Calculation of the ^2S Autoionization State of He$^-$

A. Temkin and A. K. Bhatia
National Aeronautics and Space Administration, Goddard Space Flight Center,
Greenbelt, Maryland 20771

and

J. N. Bardsley
Department of Physics, University of Pittsburgh, Pittsburgh, Pennsylvania 15213

(Received 10 December 1971)

A method is presented to remedy the defects of the projection-operator technique for calculating electron resonances in scattering from many-electron targets. Specifically it is shown that if the projection operator (i.e., idempotent) Q is replaced by a quasi-projection operator $\hat{Q}$ such that $\lim \hat{Q}\Psi = 0$ as any $r_i \to \infty$, then the spectrum of $\hat{Q}H\hat{Q}$ is discrete, and can be made to be in essentially a unique correspondence with resonance energies. Relaxation of the idempotency requirement allows us to define two forms of $\hat{Q}$ operator. The simpler of the two forms is tested on e-H and e-He$^+$ systems; the two lowest resonant energies differ by less than 0.01 eV from rigorous QHQ results. For many-electron targets it is further argued that replacement of the exact target eigenfunction (φ_0) by reasonable approximations ($\bar{\varphi}_0$) in constructing $\hat{Q}$ will affect neither the discreteness of the spectrum $\hat{Q}H\hat{Q}$ nor the proximity of its eigenvalues to the resonant energies. Calculations of He$^-$ using two different (open and closed shell) φ_0's and an angle-independent total wave function as well as a configuration-interaction wave function containing up to 40 configurations are carried out. The difference between open- and closed-shell ground-states results is about 0.02 eV, and the latter yields $E_{\text{res}}\,(^2S) = 19.363$ eV plus a width $\Gamma = 0.014$ eV. No other resonances are found below the first excited ($2\,^3S$) He threshold.

I. INTRODUCTION

The most clean-cut technique for calculating resonances in electron collisions with atomic systems arises from the projection-operator formalism of Feshbach.[1] The effectiveness of the method stems from the fact that "Feshbach" resonace energies E_n, which are part of a continuous spectrum (region of scattering solutions) of the Schrödinger equation, are in a unique correspondence with eigenvalues of a projected Schrödinger-like equation whose spectrum is discrete and which can be solved as an ordinary bound-state problem. Specifically this means that resonant energies emerge automatically from the calculation and do not have to be hunted for (and perhaps missed) as in a scattering calculation.

The projected problem $QHQ\Phi_n = \mathcal{E}_n \Phi_n$ depends on an operator Q whose complement

$$P = 1 - Q \tag{1.1}$$

is such that it does not change the asymptotic form of the exact (scattering) solution

$$\lim P\Psi = \Psi \quad \text{as} \quad r_1 \to \infty \;, \tag{1.2a}$$

so that

$$\lim Q\Psi = 0 \quad \text{as} \quad r_1 \to \infty \;. \tag{1.2b}$$

To these Feshbach[1] has added the requirement of idempotency,

$$P^2 = P \;, \quad Q^2 = Q \;, \tag{1.3}$$

which is equivalent to the statement that Q and P are projection operators.

Rigorous calculations using the formalism are restricted to one-body targets, because only in that case can explicit and rigorous P and Q operators be given.[2] In the case of many-electron targets, Feshbach[1] has given a formal expression for these operators which is not really practical because (a) it requires knowledge of the exact target wave function $\varphi_0(1, 2, \ldots, N)$, and (b) it requires the eigensolutions of a homogeneous integral equation to take care of the antisymmetric identity of scattered and orbital electrons. Problem (a) is common to any scattering problem; in practice it can be handled by using a suitable approximation of φ_0. However, problem (b) makes it impractical to use Feshbach's Q for anything but a separable approximation of φ_0.

II. QUASI-PROJECTION OPERATORS

This has led us to reexamine the idempotency requirement. Some consideration shows that the asymptotic conditions (1.2) can be satisfied by $\hat{P}$ and $\hat{Q}$ which are *not* projection operators. Furthermore one can show (cf. Appendix A) that the counterpart of condition (1.2b):

$$\lim \hat{Q}\Psi = 0 \quad \text{as any} \quad r_i \to \infty \tag{2.1}$$

leads to a discrete spectrum associated with the Rayleigh-Ritz variational principle

$$\delta \frac{\langle \hat{Q}\Psi, H\hat{Q}\Psi\rangle}{\langle \hat{Q}\Psi, \hat{Q}\Psi\rangle} = 0 \ . \tag{2.2}$$

In fact the restriction of a trial set of functions to be quadratically integrable is implicitly equivalent to using a quasi-projection operator on a totality of wave functions which might otherwise include nonvanishing scattering wave functions. In accord with our general theorem, this implicit restriction of quadratically integrable function leads to the well-known and obvious result that diagonalizing the Hamiltonian yields a discrete spectrum of energies. Such a naive procedure yields mostly nonautoionizing states, and methods of picking out the autoionization states from among them have been developed by Holøien and Midtal,[3] Lipsky and Russek,[4] Taylor and co-workers,[5] and Perkins.[6] These methods generally go under the name stabilization of roots; unfortunately with the exception of Perkins work[5] (which rigorously applies only to one-electron targets) they do not correspond to an exact prescription nor do they distinguish between Feshbach resonances (i.e., compound atom or core excited) and shape resonances. Furthermore, aside from the work of Hazi and co-workers[5,7] one does not get a prescription for the width from this formalism. And finally all these methods implicitly assume the use of a configuration-interaction-type wave function.

These difficulties derive basically from the fact that $\hat{Q}$ in these methods is not only implicit but uncontrolled and, therefore, not necessarily fixed from one approximation to the next. The idea that we shall project puts forward explicit forms for $\hat{Q}$. Once a form of $\hat{Q}$ is given, all the difficulties mentioned above can be readily overcome. Two forms of $\hat{Q}$ readily present themselves[8]

$$\hat{Q}_a \equiv \prod_{i=1}^{N+1} (1 - P_i) \tag{2.3}$$

and

$$\hat{Q}_b \equiv 1 - \sum_{i=1}^{N+1} P_i \ . \tag{2.4}$$

In both cases we define

$$\hat{P}_{a,b} \equiv 1 - \hat{Q}_{a,b} \ , \tag{2.5}$$

and the projectors P_i are given by

$$P_i = \sum_{M_L, M_S} \varphi_0(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{N+1})\rangle\!\rangle \times \langle \varphi_0(x_1, \ldots, x_{i-1}, x_{i+1}, \ldots, x_{N+1}) \ . \tag{2.6}$$

An examination will show that both Q's satisfy the asymptotic conditions on Eq. (2.1) in the energy domain in which only elastic scattering is allowed. Note that the subscript labeling P_i refers to the particle coordinates which are absent from the φ_0. Thus, i labels the scattered particle. The x refers to both spatial and spin (one-half) coordinates of each electron. The explicit inclusion of spin in these operators makes them applicable in principle to many-body targets in contrast to Feshbach's form,[1] which in addition to the difficulties mentioned above also appears to depend only on spatial coordinates. Notwithstanding this, $\hat{Q}_a$ is more complicated to use, particularly if one contemplates increasing the accuracy of φ_0 as well as Ψ.

In using $\hat{Q}_b$ we shall see directly below that in the discrete set of states associated with $\hat{Q}_b H \hat{Q}_b$ there may be states which do not correspond to autoionization states. *However there are only a finite number of such spurious states, and they can be identified in advance.*

III. ONE-ELECTRON TARGETS

To see this, consider the one-electron-target case in which the total wave function can be written

$$\Psi(x_1, x_2) = \Phi(\vec{r}_1, \vec{r}_2)\chi_S(1,2) \ , \tag{3.1}$$

where χ_s is the total singlet ($S=0$) or triplet ($S=1$) spin function. In calculating the variational principle (2.2), one will be led to calculate matrix elements of $\hat{Q}_b$ (called $\hat{Q}$ hereinafter) between two different functions $\langle \Psi_1 \hat{Q} \Psi_2\rangle$, where Ψ_1 and Ψ_2 are of the form of (3.1). [$\Psi_2\rangle$ can be considered to be $HQ\Psi\rangle$ of Eq. (2.2) for example.] Let us expand the spatial functions Φ_i associated with Ψ_i in terms of a complete set of product-target eigenstates $\vartheta_n(r)$:

$$\Phi_i = \sum_n C_{nn}^{(i)} \vartheta_n(\vec{r}_1)\vartheta_n(\vec{r}_2)\delta_{S0} + \sum_{n>\nu}\sum C_{n\nu}^{(i)}[\vartheta_n(\vec{r}_1)\vartheta_\nu(\vec{r}_2) \pm \vartheta_n(\vec{r}_2)\vartheta_\nu(\vec{r}_1)] \ , \tag{3.2}$$

where δ_{S0} explicitly indicates that the diagonal terms only arise in singlet states, and the $+(-)$ sign refers to singlet (triplet) states.

Straightforward substitution of (3.1) and (3.2) into $\langle \Psi_1 \hat{Q} \Psi_2\rangle$ leads to

$$\langle \Psi_1 \hat{Q} \Psi_2\rangle = \langle \Phi_1 \Phi_2\rangle_{12} - \langle\langle \Phi\vartheta_0\rangle_1, \langle \vartheta_0 \Phi\rangle_1\rangle_2 \ , \tag{3.3}$$

where $\hat{Q}$ from (2.4) has been used and is explicitly for $N=2$

$$\hat{Q} = 1 - P_1 - P_2 \ . \tag{2.4$'$}$$

In (3.3) the subscripts on the kets indicates the integrated coordinate in the integral symbolized by the bra-ket. Now substituting (3.2) and (3.3) we obtain after some manipulation,

$$\langle \Psi_1 \hat{Q} \Psi_2 \rangle = -C_{00}^{(1)} C_{00}^{(2)} \delta_{S0} + \sum_{n \geq \nu > 0}\sum C_{n\nu}^{(1)} C_{n\nu}^{(2)} \quad . \tag{3.4}$$

This says that arbitrary matrix elements of $\hat{Q}$ contain only one term referring to the ground state in the singlet case ($S=0$) and no terms in the triplet case ($S=1$). Thus in the singlet eigenvector spectrum there will be one eigenvector with the ground-state coefficient large; for all other eigenvectors that coefficient will be small. All other coefficients referring to the ground state in the expansion do not even arise in the calculation (i.e., are zero). The corresponding eigenvalue spectrum will, therefore, reflect that fact by having one low eigenvalue corresponding to ordinary elastic scattering (or a true bound state of the compound system, as the case may be). All remaining eigenvalues refer to doubly excited (i.e., autoionization) states. In the triplet case there are no spurious states, and in fact the operator $\hat{Q}$ then becomes identical to the idempotent Q of Hahn *et al.*[2]

The general statement is that the number of terms in $\langle \Psi_1 \hat{Q} \Psi_2 \rangle$ with indices referring to the ground state of the target is the number of spurious *autoionization* states in $\hat{Q}H\hat{Q}$, and they are the lowest ones that arise. We shall reexamine what this number is in the e-He system below. In Table I we give results for ^1S autoionization states of the e-He$^+$ and e-He systems using a Hylleraas form for Φ:

$$\Phi(\vec{r}_1, \vec{r}_2) = e^{-\gamma(r_1+r_2)} \sum_{lmn}^{\mathfrak{N}} C_{lmn}(r_1^l r_2^m + r_1^m r_2^l) r_{12}^n \quad . \tag{3.5}$$

The second and third eigenvalues then correspond to the first two resonant energies. Note both the convergence as function of the number of terms $\mathfrak{N}$ and the proximity of the essentially converged 50-term values to precision, rigorous Q-operator results.[9] (E_0 is the ground-state energy of He$^+$ and H, respectively.)

IV. TWO-ELECTRON TARGETS

We now turn to the electron-helium system which is of chief interest here, because it is the simplest example of a more than one-electron target. We consider in particular the doublet states which are the only ones that can nonrelativistically autoionize below the first excited states (2^3S) of helium. The doublet functions can be written

$$\Psi = 3^{-1/2} \sum_{\text{cyclic}} \Phi(\vec{r}_i, \vec{r}_j; \vec{r}_k) \chi_0(ij) \chi_{1/2}(k) \quad , \tag{4.1}$$

where χ_0 and $\chi_{1/2}$ are the spin-0 function (of particles i and j) and spin-$\frac{1}{2}$ function of particle k, respectively. The sum goes over cyclic permutations of i, j, k, and the spatial function is again labelled by Φ, but here it is a function of three vectors $\vec{r}_i$, $\vec{r}_j$, $\vec{r}_k$. It can be constructed to be an eigenfunction of whatever angular momentum L one chooses to make it, so that the quantum states it describes are appropriately labeled ^2L. Finally in order for Ψ to be completely antisymmetric, Φ must be symmetric in its first two arguments:

$$\Phi(\vec{r}_i, \vec{r}_j; \vec{r}_k) = +\Phi(\vec{r}_j, \vec{r}_i; \vec{r}_k) \quad . \tag{4.2}$$

We now want to determine $\langle \Psi_1 \hat{Q} \Psi_2 \rangle$ where in the present case

$$\hat{Q} = 1 - P_1 - P_2 - P_3 \quad . \tag{2.4$''$}$$

Again straightforward reduction including spin inner products leads to

$$\begin{aligned}
\langle \Psi_1 \hat{Q} \Psi_2 \rangle = {} & \langle \Phi_1(12;3) \Phi_2(12;3) \rangle - \langle \Phi_1(12;3) \Phi_2(23;1) \rangle \\
& - \{ \langle \langle \Phi_1(12;3) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(12;3) \rangle \rangle \\
& - \langle \langle \Phi_1(23;1) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(12;3) \rangle \rangle \\
& - \langle \langle \Phi_1(12;3) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(23;1) \rangle \rangle \\
& + \langle \langle \Phi_1(23;1) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(23;1) \rangle \rangle \} \quad ,
\end{aligned} \tag{4.3}$$

where φ_0 is here only a spatial function. To analyze this further we expand Φ in terms of a complete set of helium eigenstates φ_n and associated one-particle functions ϑ_m:

$$\Phi_i(12;3) = \sum_{n,m} C_{nm}^{(i)} \varphi_n(\vec{r}_1, \vec{r}_2) \vartheta_m(\vec{r}_3) \quad , \tag{4.4a}$$

which in an obvious notation we rewrite

$$\Phi_i(12;3) = \sum_{n,m} C_{nm}^{(i)} \Phi_{nm}(12;3) \quad . \tag{4.4b}$$

We now make a basic assertion which is motivated by the fact that φ_0 is largely $(1s)^2$ in character, so that by the exclusion principle no ϑ_m in (4.4a) will contribute to any process if it too is $(1s)$ (i.e., nodeless) in character. Under these circumstances the ϑ_m being used in (4.4) can always be selected such that (for all m)

$$\int \vartheta_m(\vec{r}_i) \varphi_0(\vec{r}_1, \vec{r}_2) d\mathrm{r}_i = 0 \ , \quad i = 1, 2 \ . \tag{4.5}$$

According to our basic criterion we must examine (4.3) for terms connecting to the ground state: i.e., when Φ_1, Φ_2 are replaced by $C_{0m}^{(1)} \Phi_{0m}$ and $C_{0\mu}^{(2)} \Phi_{0\mu}$, respectively. Again straightforward substitution yields

$$\langle \Phi_1(12;3) \Phi_2(12;3) \rangle_{0m,0\mu} = C_{0m}^{(1)} C_{0\mu}^{(2)} \delta_{m\mu} \quad , \tag{4.6}$$

$$\langle \langle \Phi_1(12;3) \varphi_0(12) \rangle \langle \varphi_0(12) \Phi_2(12;3) \rangle \rangle_{0m,0\mu} = C_{0m}^{(1)} C_{0\mu}^{(2)} \delta_{m\mu} \quad . \tag{4.7}$$

All other terms in (4.3) give zero when (4.5) is used. Thus, we find

$$\langle \Psi_1 \hat{Q} \Psi_2 \rangle_{0m,0\mu} = (C_{0m}^{(1)} C_{0\mu}^{(2)} - C_{0m}^{(1)} C_{0\mu}^{(2)}) \delta_{m\mu} = 0 \quad . \tag{4.8}$$

In other words $\hat{Q}(=\hat{Q}_b)$ contains *no* spurious states in the helium case.

In Appendix B we have shown that if a closed-shell target function is represented by a single

Slater determinant, then $\hat{Q}_a = \hat{Q}_b$, and for both, $\hat{Q}^2 = \hat{Q}$, which implies $P^2 = P$.[10] Thus, there are never any spurious eigenvalues for closed-shell targets. Although we have not shown it except in the case of helium, we believe that this absence of spurious eigenvalues holds even if one represents the closed-shell atom or ion by a more elaborate wave function than a single Slater determinant. Finally, one can show that if one uses the quasi-projection operator $\hat{Q}_a$, it will eliminate all spurious autoionization states below the first excited state of any target atom or ion (Appendix C).

What about the necessity of using an approximate ground state $\tilde{\varphi}_0$? We first point out that if one replaces the eigenfunctions φ_n of Eq. (15) by approximate orthonormal eigenfunctions $\tilde{\varphi}_n$, that all the steps go through as before and quasi-projection operators constructed from $\tilde{\varphi}_0$ will therefore eliminate all but a finite number of states containing $\tilde{\varphi}_0$. The question arises, however, whether the true ground state φ_0 which may be present in the approximate excited states, may not effectively reenter the spectrum or even worse convert it from a discrete to a continuous one.

Our answer to these questions is first to point out that the mere presence of some ground state in a function does not imply anything about the energy associated with that function. Consider for example the N-electron target system. If we take a linear combination of the approximate ground and first excited state

$$\tilde{\Psi} = C_0 \tilde{\varphi}_0 + C_1 \tilde{\varphi}_1 \quad ,$$

then the Hylleraas-Undheim theorem[11] says that the diagonalization of the N-electron Hamiltonian will yield eigenvalues $\tilde{E}_0$ and $\tilde{E}_1$ which are greater than true energies E_0 and E_1, respectively. Nevertheless, if one expands the corresponding eigenfunction $\tilde{\psi}_1$ of the first excited state, it will in general contain a nonzero amount of the true ground state φ_0. What the Hylleraas-Undheim theorem in effect guarantees is that the amount of φ_0 in $\tilde{\psi}_1$ is sufficiently small so as not to ruin the bound.

TABLE I. ^1S eigenvalues (in eV) of $\hat{Q}H\hat{Q}$ for one-electron targets. E_0 is the ground-state energy of the target system.

System	e-He$^+$		e-H
$\mathfrak{N}$	$\hat{\mathcal{E}}_2 - E_0$	$\hat{\mathcal{E}}_3 - E_0$	$\hat{\mathcal{E}}_2 - E_0$
13	33.2415	37.506	9.5607
22	33.2290	37.4825	9.5431
34	33.2281	37.4785	9.5410
50	33.2278	37.478	9.5406
Precision[a] QHQ	33.2267	37.471	9.5387

[a] Based on a 50-term Hylleraas calculation of Bhatia, Temkin, and Perkins, Ref. 9.

The above example is not rigorously applicable to the case at hand, because it requires the diagonalization for both eigenvalues be done simultaneously,[12] and it is confined to the N-electron problem, whereas here we go from the N to the $(N+1)$-electron system.

This question has been further studied by Hahn.[12] By explicit calculation he has shown in the ^1S e-H system that simple orthogonalization to an approximate ground state can produce an excited-target-state energy *below* the true excited-state energy. In those cases the H$^-$ autoionization-state energies can also appear below the true excited-state energy, even though with his crude total wave function there should be no such autoionization states. However even in those cases the ordering is never reversed, i.e., the autoionization-state energies always appear *below* the lowest excited-state energy associated with a function orthogonal to the approximate ground state.

It is clear, therefore, that the intelligent thing to do in judging the reality of an autoionization state is to compare its energy with the lowest energy one can achieve with an ansatz orthogonal to the approximate ground state being used. Hahn[12] has further argued that simple orthogonalization will prevent the excited state from descending too far below the true excited state.

Before turning to the calculations we make one final point to make more credible the fact that (2.2) can give rise to a discrete spectrum even when $\tilde{\varphi}_0$ used in Q is not exact. The calculational problem defined by (2.2) is a completely different one from the variational principle for H itself. Even if one used an exact solution of $H\Psi = E\Psi$ there is no reason to expect that it would have any special minimal or stationary properties with respect to (2.2). To be sure there will be extra energy shifts associated with the use of $\hat{Q}$ (in place of Q) and with the use of $\tilde{\varphi}_0$ (in place of φ_0), however, one has every right to believe these shifts will be small providing the approximations are reasonable. A *minimum* condition for a reasonable $\tilde{\varphi}_0$ is that its energy $\tilde{E}_0$ is such that

$$E_0 \leqslant \tilde{E}_0 \ll E_1 \ . \tag{4.9}$$

V. CALCULATED RESULTS, *e*-He SYSTEM

We have done two independent sets of calculations for the autoionization states of He$^-$ below the first excited state ($2\,^3S$) of He. The first is strictly for ^2S states using an angle-independent spatial function:

$$\Phi(\vec{r}_1, \vec{r}_2; \vec{r}_3) = e^{-[\alpha(r_1+r_2)+\gamma r_3]} \sum_{lmn}^{\mathfrak{N}} C_{lmn}(r_1^l r_2^m + r_1^m r_2^l) r_3^n \quad , \tag{5.1}$$

and two forms of the He (^1S) ground state, a closed

TABLE II. ^2S autoionization state of He$^-$ using angle-independent wave function (5.1). Results in eV; nonlinear parameters optimized only for the $\mathfrak{N}=70$-term results.

$\mathfrak{N}$	$\tilde{\varphi}_0 \rightarrow$	$\hat{\mathcal{E}}_1-E_0$ Closed	$\hat{\mathcal{E}}_1-E_0$ Open	Γ Closed	Γ Open
10		20.55	20.66	0.0087	0.0092
22		20.14	20.14	0.0029	0.0054
34		20.06	20.05	0.0044	0.0027
50		20.02	20.01	0.0039	0.0053
70		19.99	19.98	0.0044	0.1553

shell

$$\tilde{\varphi}_0^{(\text{closed})}=e^{-27(r_1+r_2)/16} \tag{5.2}$$

and an open shell[13]

$$\tilde{\varphi}_0^{(\text{open})}=\left[e^{-(2.1832r_1+1.1886r_2)}+(1\rightleftarrows 2)\right] \cdot \tag{5.3}$$

The purpose of this first set of calculations was to confirm that the lowest eigenvalue was convergent to a value well in the continuum of the e-He spectrum and to ascertain that the results were reasonably insensitive of the form of the ground state. For it is to be emphasized that, in spite of its simplicity, the open shell $\tilde{\varphi}_0$ of Eq. (5.3) is truly nonseparable, and cannot even be expressed as a single Slater determinant. Furthermore the ground-state energies coming from these two functions are quite different from each other.

$$\tilde{E}_0^{(\text{closed})}=-77.476 \text{ eV} , \quad \tilde{E}_0^{(\text{open})}=-78.234 \text{ eV} .$$

Nevertheless, the actual results, given in Table II, relative to the "exact" ground-state energy[14] $E_0=-79.0016$ eV reveal amazing insensitivity to these differences. The results are also significant, because, to our knowledge, they are the first completely free variational calculations [it is emphasized that no restrictions whatsoever are put on the parameters in (5.1)] for a more than one-electron target which converge to a nonzero value in the continuous spectrum. (This statement is intended to apply only to Rayleigh-Ritz-type methods applied to noncomplex energy calculations.)

It is to be emphasized in this connection that the energy of these initial calculations would not allow us to predict such a resonance, because it is above the first excited ($2\,^3S$) state[14] of He ($E_1=19.8282$ eV). [Note that since the first excited ($2\,^3S$) state of He has opposite symmetry from the ground state ($1\,^1S$), any portion of the excited state in (5.1) must correspond to an energy equal to or greater than the true excited state.] Thus, we can be sure in the angle-independent approximation that $\hat{Q}\Phi$ describes primarily scattering from the $2\,^3S$ state. Despite this fact we know very well both experimentally and from the extended calculations to be described below that a resonance does exist below the $2\,^3S$ state, it being the Schulz[15] resonance at 19.3 eV. It is not unreasonable to expect that some component of the angle-independent $\hat{Q}\Phi$ is trying to represent that resonance. With that assumption we have calculated the width using the general formula[16]

$$\Gamma=2k\,|\langle\hat{P}\Psi'|H|\hat{Q}\Psi\rangle|^2 \ . \tag{5.4}$$

In this formula $\hat{Q}\Psi$ is the resonant function associated with (5.1) and (2.5b). The nonresonant scattering function Ψ' is taken to be of the exchange approximate form; i.e., Φ in (4.1) is replaced by Φ':

$$\Phi'(\vec{r}_1,\vec{r}_2;\vec{r}_3)=\tilde{\varphi}_0(\vec{r}_1,\vec{r}_2)[u(r_3)/r_3] \ . \tag{5.5}$$

The scattered orbital $u(r_3)$ is determined from the exchange-approximation integrodifferential equation,[17] and the normalization assumed in (5.4) is[16] (rydberg units are used throughout)

$$\lim_{r\to\infty} u(r)=\frac{1}{k}\sin(kr+\eta) \ ; \tag{5.6}$$

k^2 is the scattering energy at resonance:

$$k^2=\hat{\mathcal{E}}_1-E_0 \ . \tag{5.7}$$

(Differences between the exact and approximate ground-state energy are negligible as far as the nonresonant continuum problem is concerned.) Finally the form of $\tilde{\varphi}_0$ used in deriving the scattering equation is the same one for which each resonance calculation is done.

The results shown in Table II do bear out the expectation that the widths are rather insensitive to the form of the ground state used (as long as it is used consistently). However by the time one reaches $\mathfrak{N}=70$ terms, the $\hat{Q}\Phi$ has become almost completely continuum in character, and there is no longer any resemblance between the closed-shell or open-shell widths or between the latter and experiment. Thus, these width results should be considered suggestive as to their dependence on the form of the approximate ground state.

Since our purpose has been to construct a variationally sound, interpretatively unambiguous, and hence, predictive method of computing resonances, we have therefore undertaken a second set of calculations which we now describe based on a much more general wave function than (5.1).

The wave function is a general configuration-interaction wave function which can be written

$$\Psi_{L,S=1/2}=3^{-1/2}\sum_{\{n\}}\mathcal{A}\{C_{\{n\}}R_{n_1}(r_1)R_{n_2}(r_2)R_{n_3}(r_3) \times\mathcal{Y}(l_il_jL_1;l_k;L)\mathcal{S}(\tfrac{1}{2}\tfrac{1}{2}S_1;\tfrac{1}{2};\tfrac{1}{2})\} \ . \tag{5.8}$$

Here $\mathcal{A}$ is the antisymmetrizer; $\mathcal{Y}$ are the orbital angular eigenfunctions describing particles 1 and 2 coupled to give L_1, which in turn is coupled to the l_3 of the third electron to give the total orbital angular momentum of the state L; similarly S represents the total spin—except here there are only two possible values of the intermediate spin $S_1 = 0, 1$. For $S_1=0$, (5.8) is of the general form of (4.1), and the spatial function must be symmetric in its first two arguments (4.2). If $S_1=1$, however, the spatial function is antisymmetric in its first two arguments.

The radial orbitals have the Slater form

$$R_n(r) = e^{-\alpha r} r^{n-1} \quad . \tag{5.9}$$

In general there are as many linear parameters as there are sets $\{n\}$ where

$$\{n\} \equiv \{n_1 n_2 n_3;\, (l_1 l_2) L_1, l_3;\, S_1, L\} \quad . \tag{5.10}$$

For each (unantisymmetrized) term there are in principle three nonlinear parameters, however this choice is somewhat restricted by the requirement that the term does not vanish when antisymmetrized [for example we know trivially that all the $n_i l_i$ and α of the orbitals in (5.8) cannot be the same]. In practice the number of nonlinear parameters used is very much smaller than the maximum, but nevertheless, of sufficient number to give accurate results.

For the above type of wave functions the basic program for diagonalizing H is due to Browne and Matsen.[18] It is of interest to note that the modification of the original program from H to $\hat{Q}H\hat{Q}$ consisted of adding about 100 IBM cards. The program automatically searches in the nonlinear parameter space chosen for the minimum of a specified root. An example of results of an intermediate calculation using the open-shell ground state (5.3) based on a 12-configuration expansion is given in Table III. This table shows that the expansion contained seven nonlinear parameters (1s, 2s, 3s, 2p, 3p, 4s, 4p) of which three (3s, 4s, 4p) were varied in this calculation. The program automatically varies the particular nonlinear parameters in order to minimize a specific eigenvalue, in this case the first. One can see that the eigenvalue has been lowered decisively below the $2\,^3S$ threshold and is already within 0.1 eV of the experimental value[19]

$$\mathcal{E}_{\text{expt}}(^2S) - E_0 = 19.31 \pm 0.03 \text{ eV} \quad . \tag{5.11}$$

In order to be sure that this result does indeed correspond to a resonance, it is necessary to find the lowest $2\,^1S$ energy obtainable from a function orthogonal to the approximate $\tilde{\varphi}_0$ of our calculation. As stated above this is necessary, because if such an energy were below the $2\,^3S$ threshold and below our calculated $\hat{Q}H\hat{Q}$, then our $\hat{Q}\Phi$ would have to be interpreted as describing elastic scattering from such a lowered $2\,^1S$ state and it could not be interpreted as a resonance.

TABLE III. ^2S autoionization state of He$^-$ using 12-configuration-interaction wave function (5.3). Results (in eV) based on a 12-configuration expansion $1s(2s)^2$ $1s(2s3s)$ $1s(2p)^2$ $(1s2p)\,3p$ $(1s2s)4s$ $1s(2s4s)$ $(1s2s)3s$ $1s(3s)^2$ $(1s2p)4p$ $1s(2p4p)$ $1s(3p)^2$ $1s(2p3p)$. This table gives results with respect to the variations of the nonlinear parameters specified. The remaining nonlinear parameters were approximately optimized from previous calculations and had the values $\alpha_{1s}=1.995$, $\alpha_{2s}=0.5508$, $\alpha_{2p}=0.6008$, and $\alpha_{3p}=0.4455$.

α_{3s}	$\hat{\mathcal{E}}_1 - E_0$	α_{4s}	$\hat{\mathcal{E}}_1 - E_0$	α_{4p}	$\mathcal{E}_1 - E_0$
0.3378	19.4232	0.9743	19.4206	0.4973	19.42033
0.3412	19.4227	0.9837	19.4205	0.5023	19.42028
0.3446	19.4223	0.9930	19.4204		
0.3480	19.4219	1.0024	19.4203		
0.3514	19.4217				
0.3548	19.4215				
0.3582	19.4214				
0.3617	19.4214				

We have done a reasonably definitve calculation of this energy. In fact such a calculation can be done in terms of an idempotent projection operator $q(12)$, where

$$q(12) \equiv 1 - \tilde{\varphi}_0\rangle\langle\tilde{\varphi}_0 \quad ,$$

by minimizing

$$\delta \frac{\langle q\Psi H q\Psi\rangle}{\langle\Psi q\Psi\rangle} = 0 \quad .$$

Note that this is strictly an $N=2$ particle problem [as opposed to (2.2)]. Using the Hylleraas form, (3.5), for Ψ we obtain a minimum for $\mathfrak{N}=50$ terms at $\gamma \cong 1.2$ corresponding to

$$\tilde{E}_{2\,^1S} - E_0 = 20.601 \text{ eV} \quad .$$

This is indeed above the $2\,^3S$ threshold (but it is slightly below the exact $2\,^1S$ threshold at 20.614 eV).[14] Thus, we can be sure that these eigenstates do not correspond to scattering from the $2\,^1S$ state either.

Final results are given in Table IV; as can be seen they go up to 40 configurations, and they have been done for both open- and closed-shell ground states. The comparison of these results and experiment is gratifying, nevertheless, they indicate that the major part of the shift comes from the inexact ground state.

Results of other calculations are given in Table IV. Of these the most significant are those of Perkins[6] and Weiss and Krauss.[20] The former is a quasirigorous upper bound of $\hat{Q}H\hat{Q}$ using an angle-independent ground state; the latter corresponds to using $\hat{Q}$ with a Hartree-Fock (HF) (closed-shell) ground state. In practice Weiss and Krauss used a 12-term configuration-interaction-type wave function with all s orbitals orthogonalized to the HF s-orbital of He. Their results are seen to compare very well with our own. From a prac-

TABLE IV. Configuration-interaction results in eV for He$^-$.

State	^2S				^2P
Physical quantity	$\hat{\mathcal{E}}-E_0$		Γ		$\hat{\mathcal{E}}-E_0$
Ground state	Open	Closed	Closed		Open[a]
Nonresonant continuum			Exchange	Exchange adiabatic	
No. of configurations					
12	19.420	19.403	0.0158	0.0151	19.959
28	...	19.388	0.0130	0.0124	19.927
40	19.386	19.363	0.0144	0.0139	19.862
Experiment	19.31 ± 0.03[b]		0.015 – 0.020[c] 0.008[d]		?
Other calculations					
Young[e]	19.67				
Perkins[f]	19.69				
Weiss and Krauss[g]	19.369				
Burke, Cooper, and Ormonde[h]	19.24		0.039		

[a] These ^2P values lie above the 2 ^3S threshold and do not correspond to resonances. The second ^2S eigenvalue lies above the same threshold (cf. text).

[b] Kuyatt, Simpson, and Mielczarek, Ref. 19.

[c] Andrick and Ehrhardt, Ref. 23.

[d] Gibson and Dolder, Ref. 21; Golden and Zecca, Ref. 22.

[e] A. D. Young, J. Phys. B 1, 1073 (1968).

[f] Second paper of Ref. 6.

[g] Reference 20.

[h] P. G. Burke, J. W. Cooper, and S. Ormondes, Phys. Rev. 183, 245 (1969).

tical point of view this probably represents the most reasonable way of applying the present formalism to many electron targets. In the case of the two-electron target one should be able to do better, and the open-shell ground-state results represent the first such attempt. The results however are somewhat unexpected in that for the angle-independent wave function, $\varphi_0^{(\text{open})}$ lowered (rather than raised) the energy (cf. Table II). It would clearly be desirable to extend these calculations to yet a better and angle-dependent approximation of φ_0.

The width has been approximately measured by several groups. Gibson and Dolder[21] and Golden and Zecca[22] have both measured $\Gamma = 0.008$ eV. The latter have estimated an error of 0.002 eV which makes their value noticeably different from the value of $\Gamma = 0.015$–0.020 eV estimated by Andrick and Ehrhardt.[23] Our own results are closer to the latter value. The variation of our results with the number of configurations indicate they are reasonably well converged. The results of Table II illustrate the dependence of the width to the form of the ground state. (Open-shell ground states are simply too laborious to be used with a configuration-interaction type Ψ for a width calculation.) In an effort to test the sensitivity to the nonresonant continuum function we have added a polarization potential $\alpha/(r^2+d^2)^2$ to the exchange-approximate equations[17] with d so chosen that the augmentation of the phase shift in this adiabatic exchange calculation just equals the augmentation obtained from a full polarized orbital calculation[24] over the exchange-approximation phase shift. The changes are seen to be small, and thus, we believe the present experimental results bracket rather than represent the true value.

Other small resonances below the first excited (2 ^3S) threshold have been reported.[19,25,21] In an effort to confirm these we have minimized the second (^2S) eigenvalue of our 40-term configuration-interaction wave function; we find $\hat{\mathcal{E}} - E_0 = 19.843$ eV, which is 0.023 eV above the 2 ^3S threshold, and hence, it does not correspond to a resonance. We have also calculated ^2P states, which results are given in Table IV; they are also seen to be above the 2 ^3S threshold.

There is a truly bound ^4P state (in the nonrelativistic limit). However its energy[26] is too high [$E(^4P) = 19.741$ eV] to be associated with the reported resonances. The autoionization lifetime of these state has been calculated to be greater than microseconds,[27] implying any shift from the above value must be utterly negligible. Thus, the existence of such resonances (assuming they are associated with the electron-helium system) remains unexplained.

Finally, it should be pointed out that with the calculation of a well-defined spectrum of autoionization states, one can (in principle) straightforwardly construct an optical potential.[1] This represents a rather attractive alternate method to the calculation of electron-atom scattering both in the resonant and nonresonant regimes.

ACKNOWLEDGMENTS

We should like to thank Dr. R. A. Bain and Dr. B. R. Junker for help with the configuration program and E. C. Sullivan for programming the exchange-approximate continuum problem.

APPENDIX A: DISCRETENESS OF SPECTRUM OF QHQ

Let us rewrite Eq. (4)

$$\mathcal{H}\Upsilon=\mathcal{E}\Upsilon \quad . \tag{A1}$$

In this form the consideration of this Appendix will be seen to apply to the Schrödinger equation itself ($\mathcal{H}=H$) as well as $\mathcal{H}=QHQ$ and $\mathcal{H}=\hat{Q}H\hat{Q}$. The last case is the one we are primarily interested in. The solutions of the above equation are assumed to be quadratically integrable (which is a somewhat stronger condition than assuming $\lim\Upsilon=0$ as $r\rightarrow\infty$). This is sufficient to guarantee that solutions belonging to two different energies are orthonormal

$$\langle\Upsilon(\mathcal{E}),\Upsilon(\mathcal{E}')\rangle=\delta_{\mathcal{E}\mathcal{E}'} \quad . \tag{A2}$$

Since the functions are quadratically integrable, the right-hand side of (A2) is strictly a Kronecker δ. This means that no matter how close $\mathcal{E}$ is to $\mathcal{E}'$ the inner product is zero unless $\mathcal{E}$ is precisely equal to $\mathcal{E}'$.

Now, contrary to what we want to demonstrate, let us assume that solutions exist for a continuous range of $\mathcal{E}$, so that Υ is a continuous function of $\mathcal{E}$. Let us further assume that Υ can be expanded in a Taylor series

$$\Upsilon(\mathcal{E}')=\Upsilon(\mathcal{E})+(\Delta\mathcal{E})\left(\frac{\partial\Upsilon(\mathcal{E}')}{\partial\mathcal{E}'}\right)_{\mathcal{E}'=\mathcal{E}}+O(\Delta\mathcal{E}^2) \ , \tag{A3}$$

where $\Delta\mathcal{E}=\mathcal{E}'-\mathcal{E}$. Substituting (A3) into (A2) yields

$$1+O(\Delta\mathcal{E})=0 \quad . \tag{A4}$$

Finally, taking the limit $\Delta\mathcal{E}\rightarrow 0$, we have the desired contradiction $1=0$.

This implies then that the values of $\mathcal{E}$ cannot form a continuum. (It does not say that the discrete values $\mathcal{E}_n$ cannot cluster arbitrarily close to each other as in fact they do in the hydrogenic bound-state problem.) This demonstration only applies for a $\hat{Q}$ operator constructed from exact target eigenfunctions.

APPENDIX B: EQUIVALENCE OF Q_a AND Q_b FOR CLOSED-SHELL TARGETS

It can be seen from (2.4) and (2.3) that the difference between $\hat{Q}_a$ and $\hat{Q}_b$ involves products of two, or more than two, distinct P_i. We shall show that

$$P_i P_j \Psi=0 \quad (i\neq j) \tag{B1}$$

when the target state from which the P_i's are constructed is a closed-shell Slater determinant. Specifically the target state is

$$\Phi^N(j^{-1})=\begin{vmatrix} \vartheta_1(\vec{r}_1)\alpha(1)\vartheta_1(\vec{r}_1)\beta(1)\cdots\vartheta_{N/2}(\vec{r}_1)\beta(1) \\ \vartheta_1(\vec{r}_{j-1})\alpha(j-1)\cdots\vartheta_{N/2}(\vec{r}_{j-1})\beta(j-1) \\ \vartheta(\vec{r}_{j+1})\alpha(j+1)\cdots\vartheta_{N/2}(\vec{r}_{j+1})\beta(j+1) \\ \vartheta_1(\vec{r}_{N+1})\alpha(N+1)\cdots\vartheta_{N/2}(\vec{r}_{N+1})\beta(N+1) \end{vmatrix} \ . \tag{B2}$$

The total wave function Ψ is arbitrary but completely antisymmetric, therefore insofar as its projection on $\Phi^N(j^{-1})$ goes, it is completely equivalent to write Ψ in the form

$$\Psi\rightarrow\left|\begin{array}{c:c} F(\vec{r}_j)\chi_\gamma(j)\ \cdots & F(\vec{r}_j)\chi_\delta(j) \\ \vdots & \hdashline \\ F(\vec{r}_j)\chi_\gamma(j) & \Phi^N(j^{-1}) \end{array}\right| \ . \tag{B3}$$

From (B3), however, it is clear since $\chi_\gamma(j)$ is either $\alpha(j)$ or $\beta(j)$ and since all radial orbitals in Φ^N are occupied, that we can choose:

$$\int F(\vec{r})\vartheta_n(\vec{r})d\vec{r}=0 \ , \quad n=1,2,\ldots,\tfrac{1}{2}N \ . \tag{B4}$$

[The nonorthogonal parts of F can only be such as to make various rows of the determinant on the right-hand side (B3) identical to each other, thus they make no contribution.]

Now by straightforward evaluation

$$P_j\Psi=\Phi^N(j^{-1})F(\vec{r}_j)\chi_\gamma(j) \ , \tag{B5}$$

so that

$$P_iP_j=\Phi^N(i^{-1})\langle\Phi^N(i^{-1})\Phi^N(j^{-1})F(\vec{r}_j)\chi_\gamma(j)\rangle \quad . \tag{B6}$$

Expand the Φ's by minors:

$$\Phi^{(N)}(i^{-1})=\sum_{\substack{m\\ \mu=1,2}}\vartheta_m(\vec{r}_j)\chi_\mu(j)\Phi^{(N-1)}_{m,\mu}(j^{-1},i^{-1})(-1)^{\mathcal{P}_{m\mu}} \ , \tag{B7a}$$

$$\Phi^{(N)}(j^{-1})=\sum_{\substack{n\\ \nu=1,2}}\vartheta_n(\vec{r}_i)\chi_\nu(i)\Phi^{(N-1)}_{n\nu}(j^{-1},i^{-1})(-1)^{\mathcal{P}_{n\nu}} \ . \tag{B7b}$$

Use the orthonormality

$$\langle\Phi^{(N-1)}_{n\nu}(j^{-1},i^{-1})\Phi^{(N-1)}_{m\mu}(j^{-1},i^{-1})\rangle=\delta_{nm}\delta_{\nu\mu} \tag{B8}$$

[which implies $(-1)^{\mathcal{P}_{m\mu}+\mathcal{P}_{n\nu}}\delta_{mn}\delta_{\mu\nu}=\delta_{mn}\delta_{\mu\nu}$ in (B6)] to obtain

$$P_iP_j\Psi=\sum_{n,\nu}\vartheta_n(\vec{r}_i)\chi_\nu(i)\langle\vartheta_n(\vec{r}_j)\chi_\nu(j)F(\vec{r}_j)\chi_\gamma(j)\rangle$$

$$=[\sum_n \vartheta_n(\vec{\mathrm{r}}_i)\langle\vartheta_n(\vec{\mathrm{r}}_j)F(\vec{\mathrm{r}}_j)\rangle]\,\chi_\gamma(j) \quad . \tag{B9}$$

And now using (B4), we have our desired result

$$P_i P_j \Psi = 0 \quad . \tag{B10}$$

This proves (B1), since

$$\hat{Q}_a - \hat{Q}_b = \sum_{\sigma=2}^{N+1} (-1)^\sigma \prod_{i,j\ldots(\mathrm{distinct})}^{\sigma} (P_i P_j \cdots) \tag{B11a}$$

and the number of distinct projectors P_i in each product starts with ($\sigma = 2$), it follows from (B10) that any larger number of distinct projectors acting on Ψ is zero. Hence we have

$$(\hat{Q}_a - \hat{Q}_b)\Psi = 0 \quad . \tag{B11b}$$

From (B10) one can also trivially show

$$\hat{Q}^2_{a,b}\Psi = \hat{Q}_{a,b}\Psi \tag{B12a}$$

and

$$\hat{P}^2_{a,b}\Psi = \hat{P}_{a,b}\Psi \quad . \tag{B12b}$$

APPENDIX C: ELIMINATION OF GROUND STATE BY $\hat{Q}_a$

Here we show that $\hat{Q}_a$ operating on any antisymmetric function $\Psi(1, 2, \ldots, N+1)$ eliminates the ground state in any subset of N-particle coordinates.

First, we note thet matrix elements of $\hat{Q}_a$ between two antisymmetric wave functions are independent of the order in which we write the product

$$\prod_{i=1}^{N+1} (1 - P_i)$$

in the definition of $\hat{Q}_a$, Eq. (2.3). Now let $(1 - P_j)$ operate on an arbitrary function χ (of no particular symmetry). Then, we find that clearly

$$\int \varphi_0(j^{-1})(1 - P_j)\chi(1, \ldots, N+1)\,dj^{-1} = 0 \quad . \tag{C1}$$

Since χ is arbitrary, we can choose it to be

$$\chi = \prod_{i\,(\neq j)} (1 - P_i)\Psi \quad , \tag{C2}$$

where Ψ is antisymmetric. Then, it is clear for the purposes of taking matrix elements that

$$(1 - P_j)\chi = \hat{Q}_a\Psi \ , \tag{C3}$$

so that (C1) becomes

$$\int \varphi_0(j^{-1})\hat{Q}_a\Psi\,dj^{-1} = 0 \quad . \tag{C4}$$

However j can be any of the indices $1, \ldots, N+1$. Thus, we have shown that $\hat{Q}_a$ eliminates the ground state of any antisymmetric function of the $(N+1)$-particle variables in any subset of N variables.

---

[1] H. Feshbach, Ann. Phys. (N. Y.) 19, 287 (1962).

[2] Y. Hahn, T. F. O'Malley, and L. Spruch, Phys. Rev. 128, 932 (1962). The explicit equivalence of P and Q in this paper to that given in Ref. 1 for a one-electron target is shown explicitly in Y. Hahn, Ref. 10.

[3] E. Holøien and J. Midtdal, J. Chem. Phys. 45, 2209 (1966), and references contained therein.

[4] L. Lipsky and A. Russek, Phys. Rev. 142, 59 (1966).

[5] I. Eliezer, H. S. Taylor, and J. K. Williams, J. Chem. Phys. 47, 2165 (1965); A. H. Hazi and H. S. Taylor, Phys. Rev. A 1, 1109 (1970).

[6] J. F. Perkins, Phys. Rev. 178, 89 (1969). Some further work attempting to extend his ideas to the two-electron target is contained in J. F. Perkins, Phys. Rev. A 4, 489 (1971).

[7] M. F. Fels and A. U. Hazi, Phys. Rev. A 4, 662 (1971); and unpublished.

[8] We are indebted to Dr. R. J. Drachman for helpful discussions on $\hat{Q}_a$.

[9] A. K. Bhatia, A. Temkin, and J. F. Perkins, Phys. Rev. 153, 177 (1967).

[10] This fact is implicit in Y. Hahn, Ann. Phys. (N.Y.) 58, 137 (1970); Phys. Rev. 187, 51 (1969).

[11] E. Hylleraas and B. Undheim, Z. Physik 65, 759 (1930).

[12] Y. Hahn, Phys. Rev. A 5, 309 (1972); we thank Dr. Y. Hahn for helpful correspondence on this point.

[13] H. Shull and P. Lowdin, J. Chem. Phys. 25, 1035 (1965).

[14] C. L. Pekeris, Phys. Rev. 112, 1649 (1958); 127, 509 (1962).

[15] G. J. Schulz, Phys. Rev. Letters 10, 104 (1963).

[16] T. F. O'Malley and S. Geltman, Phys. Rev. 137, A1344 (1965).

[17] P. M. Morse and W. P. Allis, Phys. Rev. 44, 269 (1933). The explicit form of the e-He scattering equation using a closed-shell ground state may be found in Y. Itikawa, T. Ohmura, and K. Takayanagi, Progr. Theoret. Phys. (Kyoto) 42, 993 (1969).

[18] J. C. Browne and F. A. Matsen, Phys. Rev. 136, A1227 (1964); F. A. Matsen and J. C. Browne, J. Chem. Phys. 66, 2322 (1962).

[19] C. Kuyatt, J. A. Simpson, and S. Mielczarek, Phys. Rev. 138, A385 (1965).

[20] A. Weiss and M. Krauss, J. Chem. Phys. 52, 4263 (1970).

[21] J. R. Gibson and K. T. Dolder, J. Phys. B 2, 741 (1969).

[22] D. E. Golden and A. Zecca, Rev. Sci. Instr. 42, 210 (1971).

[23] D. Andrick and H. Ehrhardt, Z. Physik 192, 99 (1966).

[24] W. Duxler, R. T. Poe, and R. W. LaBahn, Phys. Rev. A 4, 1935 (1971).

[25] D. E. Golden and A. Zecca, Phys. Rev. A 1, 241 (1970).

[26] B. Brehm, M. Gusinow, and J. L. Hall, Phys. Rev. Letters 19, 737 (1967). A value very close to this has been calculated by A. Weiss (unpublished).

[27] S. T. Manson, Phys. Rev. A 3, 147 (1971).