the sign of the scattering length. The triplet state is rather unusual. A state of negative energy does exist, but the exclusion principle rules out this state physically. In such a case the scattering theory accepts this state as legitimately bound, predicting a phase $\delta_0^- \to \pi$ as $k \to 0$ and predicting $a_- > 0$.

If both a_+ and a_- are positive, we have an upper bound on the integrated total cross section, namely

$$\int_0^\infty \sigma_t dk \leq 2\pi^2(\tfrac{1}{2}R + 2a_0). \tag{5}$$

Using the (approximate) value of R (at $E=0$) computed in reference 1, the inequality (5) becomes

$$\frac{1}{2\pi^2}\int_0^\infty \sigma_t dk \leq 7.52 a_0. \tag{6}$$

Using the most recent calculated values[6] of $a_\pm$ and the same R as above, the equality (4) becomes

$$\frac{1}{2\pi^2}\int_0^\infty \sigma_t dk = 4.5 a_0. \tag{7}$$

Two experiments, referred to as (B)[9] and (F),[10] exist which measure σ_t, and an earlier paper[1] used these measurements to compute the integral in (5). These results were

$$\begin{aligned} &\text{Experiment } (B) \quad \frac{1}{2\pi^2}\int \sigma_t dk = (10.3 \pm 0.5) a_0, \\ &\text{Experiment } (F) \quad \frac{1}{2\pi^2}\int \sigma_t dk = (5.1 \pm 0.5) a_0. \end{aligned} \tag{8}$$

It is apparent, on comparing (6) and (7) with (8), that experiment (B) violates the inequality, while experiment (F) easily satisfies the inequality, and comes reasonably close to agreeing with the equality based on existing calculations of the scattering length and our estimate of R. The indicated spread in (8) results from different choices of the cross sections outside the range of the experiments.

We conclude that knowledge of the sign of the scattering length can be used to place a limit on the integrated total cross sections, and accurate calculation of the scattering length and bound-state residue gives the value of $\int_0^\infty \sigma_t dk$. Thus there is a close relation between the scattering length, the integrated cross section, and the bound-state wave functions of the system (as reflected in the residue R).

[9] B. Bederson, J. Hammer, and H. Malamud, New York University Technical Report No. 2, Electron Scattering Project (unpublished).

[10] R. T. Brackman, W. L. Fite, and R. H. Neynaber, Phys. Rev. **112**, 1157 (1958).

PHYSICAL REVIEW VOLUME 120, NUMBER 1 OCTOBER 1, 1960

Lower Bounds for Eigenvalues with Application to the Helium Atom*

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(Received May 12, 1960; revised manuscript received June 27, 1960)

A method is derived for finding lower bounds to the energy levels of the Schrödinger equation. This method is applied to the helium atom. The best lower bounds thus obtained are -3.063_7 and -2.165_8 atomic units for the energies $E(1\,^1S)$ and $E(2\,^1S)$, respectively. If our lower bound for $E(2\,^1S)$ is used together with the best published values of $\langle H\psi,\psi\rangle$ and $\langle H\psi,H\psi\rangle$ of the ground state, a rigorous lower bound -2.9037474 atomic units is found for $E(1\,^1S)$.

I. INTRODUCTION

THE basic ideas of our procedure for lower bounds go back to the work of A. Weinstein,[1] which introduces an explicity solvable *base problem* with lower eigenvalues. Weinstein links the base problem to the given problem by a sequence of *intermediate problems* which can be solved in terms of the base problem and which improve the lower bounds. In his work on plates these problems are obtained by changing the boundary conditions. By combining his lower bounds with the upper bounds given by the Rayleigh-Ritz method he obtained an accuracy of up to 0.18%.

Later Aronszajn[2] emphasized that a base problem can be obtained by a change of the operator and outlined the construction of the intermediate problems. In this paper we simplify Aronszajn's important extension of the method of intermediate problems by constructing these problems in such a way that in order to solve them in terms of the base problem one need only

* This research was partially supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. The investigation was initiated when the author was at the National Bureau of Standards, and a resume of some of the results was published Proc. Natl. Acad. Sci. U. S. **45**, 850 (1959).

[1] A. Weinstein, Memorial des Sci. Math. No. 88 (1937).

[2] N. Aronszajn, Proceedings of the Oklahoma Symposium on Spectral Theory and Differential Problems, 179, 1951 (unpublished).

solve an algebraic equation instead of a transcendental equation which involves infinite sums.

No attempt is made to compare our method with other procedures, which may be more efficient in certain problems.

II. THE BASE PROBLEM

Let us denote the inner product by $\langle\psi,\varphi\rangle=\int\psi\varphi^*d\tau$. We are given the Schrödinger equation in the form

$$H\psi=E\psi, \tag{2.1}$$

where we assume that the lowest part of the spectrum of the Hermitian operator H consists of bound states only. An eigenfunction ψ_i corresponding to an energy E_i must satisfy

$$H\psi_i=E_i\psi_i, \qquad \langle\psi_i,\psi_j\rangle=\delta_{ij}, \tag{2.2}$$

where δ_{ij} is the Kronecker delta. We consider the energy levels to be ordered in a nondecreasing sequence $E_1\leq E_2\leq E_3\cdots$ where each degenerate energy level is repeated the number of times equal to its multiplicity. We allow the possibility of continuous energy states and bound states with energies larger than each energy E_i in the above sequence.

Rough lower bounds to the energy levels E_i can be obtained as follows. Assume that the Hamiltonian H can be written as the sum of two parts, where one of these parts H^0 is of a sufficiently simple structure that its Schrödinger equation has an exact solution. Further assume that the other part H' is a positive operator. It is not necessary that H' be small as the method of intermediate problems is not related to stationary pertubation theory.

We have

$$H=H^0+H', \tag{2.3}$$

where

$$H^0\psi_i{}^0=E_i{}^0\psi_i{}^0 \text{ and } \langle H'\psi,\psi\rangle=\int(H'\psi)\psi^*\geq 0, \text{ any } \psi. \tag{2.4}$$

Here the $E_i{}^0$ are the ordered energy levels of the lowest part of the spectrum of the operator H^0, $E_1{}^0\leq E_2{}^0\leq\cdots$. Each energy level $E_i{}^0$ is repeated in the sequence the number of times equal to its multiplicity. The eigenfunctions $\psi_i{}^0$ corresponding to the $E_i{}^0$ are considered to be orthonormalized so that

$$\langle\psi_i{}^0,\psi_j{}^0\rangle=\delta_{ij}. \tag{2.5}$$

We call the eigenvalue problem for H^0 the base problem.

The known energy levels $E_i{}^0$ of H^0 give rough lower bounds to the unknown energies E_i of H according to the basic inequalities

$$E_i{}^0\leq E_i, \qquad i=1, 2, 3\cdots. \tag{2.6}$$

The proof that $E_i{}^0\leq E_i$ follows immediately from the minimum characterization of the first eigenvalue and the inequality

$$\langle H^0\psi,\psi\rangle\leq\langle(H^0+H')\psi,\psi\rangle, \tag{2.7}$$

for arbitrary ψ. In fact,

$$E_1{}^0=\min_{\langle\psi,\psi\rangle=1}\langle H^0\psi,\psi\rangle\leq\min_{\langle\psi,\psi\rangle=1}\langle H\psi,\psi\rangle=E_1. \tag{2.8}$$

The proof of the inequalities (2.6) for all values of i follows from the maximum-minimum characterization of the eigenvalues and goes back to Weyl.[3]

III. INTERMEDIATE PROBLEMS

We now introduce a sequence of intermediate Hamiltonian operators $H^1, H^2, H^3\cdots$. Each operator H^k will approximate H in the following precise sense. It will have energy levels intermediate between those of any operator which appears earlier in the sequence and those of H. This in itself would not be very helpful if we did not have the following fundamental properties of H^k. The energy levels and eigenfunctions of H^k are, as we shall see, obtained by a k-dimensional matrix problem which is explicitly solvable in terms of the known energy levels and eigenfunctions of H^0.

To define H^k with these properties we temporarily introduce a second scalar product $\langle\langle\varphi,\psi\rangle\rangle$ defined by

$$\langle\langle\varphi,\psi\rangle\rangle=\int(H'\varphi)\psi^*d\tau=\langle H'\varphi,\psi\rangle. \tag{3.1}$$

Here we restrict φ and ψ so that $H'\varphi\neq 0$ and $H'\psi\neq 0$ for $\varphi, \psi\neq 0$. Let $p_1, p_2, p_3\cdots$ be an arbitrarily chosen sequence of linearly independent, not necessarily orthogonal, elements in the vector space with scalar product $\langle\langle\varphi,\psi\rangle\rangle$. Using this new scalar product $\langle\langle\varphi,\psi\rangle\rangle$ we compute the projection $P^k\varphi$ of an element φ on the finite space spanned by the first k vectors $p_1, \cdots, p_k$ so that

$$P^k\varphi=\sum_{i=1}^{k}c_ip_i. \tag{3.2}$$

Since $p_1, \cdots, p_k$ are not necessarily orthogonal we compute the elements c_i from the system of equations

$$\langle\langle P^k\varphi,p_j\rangle\rangle=\langle\langle\varphi,p_j\rangle\rangle=\sum_{i=1}^{k}c_i\langle\langle p_i,p_j\rangle\rangle, \quad 1\leq j\leq k. \tag{3.3}$$

If $H'\varphi=0$ we define $P^k\varphi=0$.

We define the intermediate Hamiltonian H^k by the equation

$$H^k=H^0+H'P^k, \quad 1\leq k, \tag{3.4}$$

and prove its fundamental properties.

As the projection increases in magnitude with k, we have the inequalities

$$0\leq\langle\langle P^k\psi,P^k\psi\rangle\rangle\leq\langle\langle P^{k+t}\psi,P^{k+t}\psi\rangle\rangle\leq\langle\langle\psi,\psi\rangle\rangle, \quad k, t=1, 2, 3\cdots. \tag{3.5}$$

[3] H. Weyl, Bull. Am. Math. Soc. **56**, 115 (1950).

or equivalently

$$\langle H^0\psi,\psi\rangle\leq\langle H^k\psi,\psi\rangle\leq\langle H^{k+t}\psi,\psi\rangle\leq\langle H\psi,\psi\rangle, \quad k,\ t=1,\ 2,\ 3,\ \cdots. \tag{3.6}$$

If we denote the ordered energy levels of H^k by $E_1{}^k\leq E_2{}^k\leq E_3{}^k\ \cdots$ then the inequalities (3.6) assure that

$$E_i{}^0\leq E_i{}^k\leq E_i{}^{k+t}\leq E_i, \quad i,\ k,\ t=1,\ 2,\ 3\ \cdots. \tag{3.7}$$

As in Eq. (2.6), the proof of (3.7) follows from the maximum-minimum characterization of the eigenvalues. The inequalities (3.7) justify the name of intermediate problems.

IV. SOLUTION OF THE INTERMEDIATE PROBLEMS

In order to determine the energy levels of H^k starting from the energy levels of H^0 we first find an explicit expression for H^k. Equations (3.2) and (3.3) show that for arbitrary ψ

$$H'P^k\psi=\sum_{i=1}^{k} c_iH'p_i, \tag{4.1}$$

where the c_i are determined as

$$c_i=\sum_{j=1}^{k} b_{ji}\langle H'\psi,p_j\rangle, \quad 1\leq i\leq k, \tag{4.2}$$

and (b_{ji}) is the matrix inverse to that with elements $\langle H'p_j,p_i\rangle$. We combine (4.1), (4.2), and (3.4) to see that the operator H^k becomes

$$H^k\psi=H^0\psi+\sum_{i=1}^{k}\sum_{j=1}^{k}\langle\psi,H'p_j\rangle b_{ji}H'p_i. \tag{4.3}$$

To avoid essential difficulties in the discussion of the equation $H^k\psi=E\psi$, we simplify the operator H^k by a special choice of the elements p_i, $1\leq i\leq k$, which up to now were selected in an arbitrary manner.

We require that each element $\psi_i{}^0$ belong to the range of the Hamiltonian H', and we define from now on each p_i by the equation

$$H'p_i=\psi_i{}^0, \qquad i=1,\ 2,\ \cdots,\ k. \tag{4.4}$$

This special choice of the elements p_i is usually possible and distinguishes our procedure from that of Aronszajn.[4] If H' is positive definite then the Hamiltonian $(H')^{-1}$ satisfying the relationships $(H')^{-1}H'=H'(H')^{-1}=I$ (I the identity operator) exists, and we can equivalently write (4.4) in the form

$$p_i=(H')^{-1}\psi_i{}^0, \qquad i=1,\ \cdots,\ k. \tag{4.5}$$

[4] It turns out that our sequence has the properties of the distinguished sequences of A. Weinstein in 1937. In a forthcoming paper by the author and D. W. Fox a new procedure for an arbitrary choice of the p_i's has been developed.

The operator H^k now becomes

$$H^k\psi=H^0\psi+\sum_{i=1}^{k}\sum_{j=1}^{k}\langle\psi,\psi_j{}^0\rangle b_{ji}\psi_i{}^0,$$

so that the equation $H^k\psi=E\psi$ can be written as

$$H^0\psi+\sum_{i=1}^{k}\sum_{j=1}^{k}\langle\psi,\psi_j{}^0\rangle b_{ji}\psi_i{}^0=E\psi, \tag{4.6}$$

where b_{ji} is the matrix inverse to that with elements $\langle\psi_i{}^0,p_j\rangle$, $H'p_j=\psi_j{}^0$.

It is now possible to discuss H^k in a simple way. In fact, let $\psi_t{}^0$ be an eigenfunction of H^0 which is not used in forming any element p_i according to (4.5). Then $H^k\psi_t{}^0=H^0\psi_t{}^0$ and $\psi_t{}^0$ is an eigenfunction $\psi_t{}^k$ of H^k; hence, the energy level $E_t{}^0$ is also an energy level $E_t{}^k$ of H^k. In a similar manner one can show that the continuous spectrum of H^k is identical to that of H^0.[5]

We now proceed to find all other eigenfunctions and energy levels of H^k. To do this we investigate whether (4.6) has solutions of the form

$$\psi_s=\sum_{t=1}^{k}\alpha_t{}^{(s)}\psi_t{}^0, \tag{4.7}$$

where each $\psi_t{}^0$ is used in defining a p_t according to (4.5). Equation (4.6) now reads

$$\sum_{t=1}^{k}\alpha_t{}^{(s)}E_t{}^0\psi_t{}^0+\sum_{i=1}^{k}\sum_{j=1}^{k}b_{ji}\alpha_j{}^{(s)}\psi_i{}^0-E\sum_{t=1}^{k}\alpha_t{}^{(s)}\psi_t{}^0=0. \tag{4.8}$$

The linear independence of the functions $\psi_t{}^0$ reduces (4.8) to

$$\sum_{j=1}^{k}\{[E_t{}^0-E]\delta_{jt}+b_{jt}\}\alpha_j{}^{(s)}=0, \quad 1\leq t\leq k, \tag{4.9}$$

where δ_{jt} is the Kronecker delta. Hence, k eigenfunctions and energy levels of H^k are found by the solution of the matrix eigenvalue problem (4.9).

Summary

The eigenvalues of the intermediate Hamiltonian H^k are given by the following rule.

(a) k of the bound states are the roots of

$$0=|\,(E_i{}^0-E)\delta_{ij}+b_{ij}\,|, \qquad 1\leq i,\ j\leq k, \tag{4.10}$$

where b_{ij} is the element of the matrix inverse to that with elements $\langle\psi_i{}^0,p_j\rangle$, $H'p_j=\psi_j{}^0$.

(b) All other bounds states of H^k are those bound states $E_t{}^0$ of H^0 whose corresponding eigenfunctions $\psi_t{}^0$ have not been used in forming the elements p_i, $1\leq i\leq k$.

(c) H^k has a continuous spectrum identical with that of H^0.

[5] For a detailed mathematical discussion of this and some other facts see the paper by N. Bazley which will appear in the January, 1961, issue of the Journal of Math. and Mech.

Since the E's determined from (4.10) are not necessarily the k lowest E's of H^k, one must reshuffle the E's in (a) and (b) into a nondecreasing sequence $E_1^k \leq E_2^k \leq E_3^k \cdots$. We then have the fundamental inequalities.

$$E_i^0 \leq E_i^k \leq E_i^{k+t} \leq E_i \qquad 1 \leq i, k, t. \tag{4.11}$$

Remark

Our method requires that H' be positive and that our choice of the elements p_i is possible. If H' is bounded below we can always choose our base problem in the following manner so that these conditions are satisfied.

Defined the Hamiltonian H_c^0 by $H_c^0 = H^0 - cI$ and the Hamiltonian H_c' by $H_c' = H' + cI$ where I is the identity operator and c is any real number satisfying

$$\langle H'\psi,\psi\rangle + c\langle\psi,\psi\rangle \geq d\langle\psi,\psi\rangle, \tag{4.12}$$

for some positive number d. Then H has the decomposition $H = H_c^0 + H_c'$ where H_c' is positive definite and it is known that $(H_c')^{-1}\psi$ exists for every vector ψ. The base problem with Hamiltonian H_c^0 has the same eigenfunctions ψ_i^0 as does H^0. Its lowest energies E_{ci}^0 are related to the E_i^0 by $E_{ci}^0 = E_i^0 - c$. The solution of the kth intermediate problem is again reduced to the evaluation of the integrals $\langle (H_c')^{-1}\psi_i^0, \psi_j^0\rangle$ for $i, j = 1, \cdots, k$.

V. GENERALIZATION

We are able to extend our method to the more general equation

$$H_1\psi_i = E_i H_2\psi_i, \tag{5.1}$$

where H_1 and H_2 are linear operators. We assume that it is possible to effect the decomposition

$$H_1 = H_1^0 + H_1', \qquad H_2 = H_2^0 - H_2', \tag{5.2}$$

where H_1', H_2', H_2^0 are positive and where

$$H_1^0\psi_i^0 = E_i^0 H_2^0\psi_i^0 \tag{5.3}$$

has known orthonormalized eigenfunctions ψ_i^0 with energy levels E_i^0; hence $E_i^0 \leq E_i$, $i = 1, 2, \cdots$.

As in the previous section, we introduce operators H_1^k and H_2^j which, respectively, approximate H_1 and H_2 so as to give intermediate lower bounds. We take $j = k$ for simplicity. The energy levels of $H_1^k\psi = E^{k,k}H_2^k\psi$ are given here by the following rule:

(a) k of the bound states are the roots of

$$0 = |(E_i^0 - E)\delta_{ij} + e_{ij} + Ef_{ij}|, \tag{5.4}$$

where e_{ij} is the matrix inverse to that with elements $\langle H_2^0\psi_i^0, p_j\rangle$, $H_1'p_j = H_2^0\psi_i$, and f_{ij} is the matrix inverse to that with elements $\langle H_2^0\psi_i^0, q_j\rangle$, $H_2'q_j = H_2^0\psi_j^0$.

(b) All other bound states are those states with energy E_i^0 whose eigenfunctions ψ_i^0 do not appear in (a).

(c) The continuous spectrum of the intermediate problem is identical with that of the base problem.

The ordered energies give lower bounds according to

$$E_i^0 \leq E_i^{k,k} \leq E_i^{k+t,k+t} \leq E_i, \quad 1 \leq i, k, t. \tag{5.5}$$

VI. APPLICATION TO THE HELIUM ATOM

The method of intermediate problems can be used to approximate the bound states of ordinary differential equations such as the radial Schrödinger equation. However, in this paper we will apply the method to the partial differential equation satisfied by the helium atom. We will neglect nuclear motion, relativistic effects, and the influence of spin. We use atomic units throughout.

Let $\mathbf{r}_1$ and $\mathbf{r}_2$ denote the position vectors of each electron with the nucleus as origin. The helium atom Hamiltonian operating on sufficiently regular functions ψ is

$$H\psi = -\tfrac{1}{2}\Delta_1\psi - \tfrac{1}{2}\Delta_2\psi - \frac{2\psi}{r_1} - \frac{2\psi}{r_2} + \frac{\psi}{r_{12}}, \tag{6.1}$$

in atomic units. Here Δ_i is the Laplacian operator in the coordinates $\mathbf{r}_i$, $i = 1, 2$. Also, $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ and $r_1 = |\mathbf{r}_1|$, $r_2 = |\mathbf{r}_2|$.

In order to take advantage of the symmetry properties of the operator (6.1), we restrict ourselves to S states of parahelium. For these states the eigenfunctions of H depend only upon r_1, r_2, and r_{12} and are symmetric in the spatial coordinates of the two electrons. Accordingly, we restrict the operator H to the subspace of the square-integrable functions which are dependent only on the variables r_1, r_2, r_{12} and which are symmetric in r_1 and r_2.

If we neglect the electron interaction term $1/r_{12}$ in (6.1), the resulting Hamiltonian

$$H^0\psi = -\tfrac{1}{2}\Delta_1\psi - \tfrac{1}{2}\Delta_2\psi - \frac{2}{r_1}\psi - \frac{2}{r_2}\psi, \tag{6.2}$$

has a well-known spectrum whose initial part is discrete and bounded below. Further, $H' = 1/r_{12}$ is a positive definite operator so that the eigenvalue problem for H^0 is suitable as a base problem.

The eigenfunctions of H^0 are given by

$$\psi_{n_1n_2l} = N[R_{n_1l}(r_1)R_{n_2l}(r_2) + R_{n_1l}(r_2)R_{n_2l}(r_1)] \times P_l(\cos\theta_{12}), \tag{6.3}$$

where the elements R_{nl} are the normalized hydrogen radial wave functions, P_l is the lth normalized Legendre polynamial, and θ_{12} is the angle between r_1 and r_2. Here N is chosen so that the eigenvectors are normalized. The corresponding energy levels are

$$-2(1/n_1^2 + 1/n_2^2), \tag{6.4}$$

each with multiplicity $\max(n_1, n_2)$. There is a spectrum of continuous energies, overlapping (6.4), from -2 to infinity. The lowest part of the spectrum of H^0 is given by

$$E_i^0 = -2(1 + 1/i^2), \quad i = 1, 2, \cdots, \tag{6.5}$$

and the corresponding eigenfunctions are

$$\psi_1^0=(1/4\pi)R_{10}(r_1)R_{10}(r_2),$$
$$\psi_i^0=(1/\sqrt{24\pi})[R_{10}(r_1)R_{i0}(r_2)+R_{10}(r_2)R_{i0}(r_1)], \quad 2\leq i. \quad (6.6)$$

Kato[6] has shown that the lowest part of the spectrum of H consists of a sequence of discrete energy levels $E(1\,^1S)\leq E(2\,^1S)\leq E(3\,^1S)\cdots$ before the presence of continuous spectrum.

Since H^0 is the base problem operator we have, by (2.6) and (6.5),

$$-4\leq E(1\,^1S), \quad -2.5\leq E(2\,^1S), \quad -20/9\leq E(3\,^1S)\cdots. \quad (6.7)$$

We now solve the first intermediate problem and choose $p_1=(r_{12}/4\pi)R_{10}(r_1)R_{10}(r_2)$. By the summary at the end of Sec. IV we see that the first intermediate problem has the lower part of its spectrum identical to that of H^0, except that the eigenvalue -4 is replaced by

$$-4+1/\langle(H')^{-1}\psi_1^0,\psi_1^0\rangle. \quad (6.8)$$

The term $\langle(H')^{-1}\psi_1^0,\psi_1^0\rangle$ is calculated in Appendix A as 1.093 750. The first intermediate problem has the ordered spectrum

$$-3.0857, \quad -2.5, \quad -20/9, \cdots. \quad (6.9)$$

Accordingly, we have shown that

$$-3.0857\leq E(1\,^1S). \quad (6.10)$$

We now solve a third intermediate problem with a projection on the terms $p_i=r_{12}\psi_i^0$, $i=1, 2, 3$. We calculate the nine matrix elements $\langle(H')^{-1}\psi_i^0,\psi_j^0\rangle$ for $i, j=1, 2, 3$. The numerical results are given in Appendix A. We then find the inverse matrix (b_{ij}) and solve the 3×3 equation

$$0=\det[(E_i^0-E)\delta_{ij}+b_{ij}], \quad i, j=1, 2, 3, \quad (6.11)$$

where $E_1^0=-4$, $E_2^0=-2.5$, and $E_3^0=-20/9$. The roots of (6.11) are

$$-3.063_7; \quad -2.165_5; \quad -2.039_2. \quad (6.12)$$

The lower part of the spectrum of this third intermediate problem still has the eigenvalues

$$-2(1+1/i^2), \quad i=4, 5, 6, \cdots. \quad (6.13)$$

Since $-2.039_2>E_4^0$ we must throw it away and use $E_4^0=-2.125$ as E_3^3. The first three ordered eigenvalues of the third intermediate problem are

$$E_1^3=-3.063_7, \quad E_2^3=-2.165_5, \quad E_3^3=-2.125. \quad (6.14)$$

We have thus shown

$$-3.063_7\leq E(1\,^1S) \quad \text{and} \quad -2.165_5\leq E(2\,^1S).$$

Using the Rayleigh-Ritz upper bounds as determined by Kinoshita[7] and Coolidge and James[8] (see also articles of Pekeris[9]) we have

$$-3.063_7\leq E(1\,^1S)\leq -2.9037237, \quad (6.15)$$

and

$$-2.165_5\leq E(2\,^1S)\leq -2.1458. \quad (6.16)$$

VII. APPLICATIONS OF INTERMEDIATE PROBLEMS TO TEMPLE'S FORMULA

The inequalities (6.15) and (6.16) could be regarded as final results, as the procedure developed here always leads in similar circumstances to lower bounds for the first and higher energy levels without recourse to any other theory. Sometimes our procedure can help to rigorously establish lower bounds by other methods. For instance, consider Temple's formula,[10]

$$E(1\,^1s)\geq\langle H\psi,\psi\rangle-\frac{\langle H\psi,H\psi\rangle-\langle H\psi,\psi\rangle^2}{E^*-\langle H\psi,\psi\rangle}. \quad (7.1)$$

This formula gives a lower bound for the first energy level $E(1\,^1S)$ provided (a) the quantities $\langle H\psi,\psi\rangle$ and $\langle H\psi,H\psi\rangle$ have been numerically computed for any normalized test function ψ, (b) a numerical bound E^* is known which satisfies the conditions

$$\langle H\psi,\psi\rangle<E^*\leq E(2\,^1S). \quad (7.2)$$

The condition (a) is met in the case of the helium atom because Kinoshita[7] computed the expressions involving ψ by taking a 80-term test function. As to the condition (b), expressed by the inequality (7.2), a numerical value for E^* can be taken as $E^*=E_2^0=-2.5$. This follows from the well known maximum-minimum theory. Actually, Kinoshita prefers to use the experimental value $E^*=-2.146$.

Our method provides for E^* the value -2.165_5. Substituting this last value into Temple's formula, we obtain the final inequality (in atomic units)

$$-2.9037474\leq E(1\,^1s)\leq -2.9037237. \quad (7.3)$$

It should be noticed that we are not able to apply Temple's formula to obtain lower bounds for $E(2\,^1s)$ without the use of intermediate problems, since no value corresponding to E^* is known from the base problem. In the case of $E(2\,^1s)$ an application of Temple's formula would require several additional computations and the solution of higher-order intermediate problems. Unless such computations are made we have to use the lower bounds given by (6.16).

VIII. APPENDIX: CALCULATION OF THE MATRIX ELEMENTS $\langle(H^1)^{-1}\psi_i^0, \psi_j^0\rangle$, $(i,j=1,2,3,)$

Our basic integrals involve the terms

$$\int_0^\infty\int_0^\infty R_{n_10}(r_1)R_{n_20}(r_2)R_{n_30}(r_1)R_{n_40}(r_2) \times I(r_1,r_2)r_1^2r_2^2dr_1dr_2, \quad (A.1)$$

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and

$$I(r_1,r_2)=\frac{1}{(4\pi)^2}\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} r_{12}\sin\theta_1 \times\sin\theta_2 d\theta_1 d\theta_2 d\varphi_1\varphi_2. \quad (A.2)$$

Now,

$$r_{12}=(r_1^2+r_2^2-2r_1r_2\cos\theta_{12}) \times\frac{1}{r_>}\left[\sum_{t=0}^{\infty}\left(\frac{r_<}{r_>}\right)^t P_t(\cos\theta_{12})\right], \quad (A.3)$$

where $r_>$ and $r_<$, respectively denote the larger and smaller of the magnitudes of r_1 and r_2. Since

$$\cos\theta_{12}P_t(\cos\theta_{12}) =\frac{t+1}{2t+1}P_{t+1}(\cos\theta_{12})+\frac{t}{2t+1}P_{t-1}(\cos\theta_{12}), \quad (A.4)$$

we rewrite (A.3) as

$$r_{12}=\sum_{t=0}^{\infty}\frac{(r_<)^t}{(r_>)^{t+1}}(r_1^2+r_2^2)P_t(\cos\theta_{12}) -\sum_{t=0}^{\infty}\frac{2r_1r_2(r_<)^t(t+1)}{(r_>)^{t+1}(2t+1)}P_{t+1}(\cos\theta_{12}) -\sum_{t=0}^{\infty}\frac{2r_1r_2(r_<)^t t}{(r_>)^{t+1}(2t+1)}P_{t-1}(\cos\theta_{12}). \quad (A.5)$$

But,

$$P_t(\cos\theta_{12})=\frac{4\pi}{2t+1}\sum_{p=-t}^{t}Y_{tp}(\theta_1,\varphi_1)\bar{Y}_{tp}(\theta_2,\varphi_2), \quad (A.6)$$

that

$$\frac{1}{(4\pi)^2}\int_0^{\pi}\int_0^{\pi}\int_0^{2\pi}\int_0^{2\pi} P_t(\cos\theta_{12})\sin\theta_1 \times\sin\theta_2 d\theta_1 d\theta_2 d\varphi_1 d\varphi_2=\delta_{t0}. \quad (A.7)$$

We combine (A.5) and (A.7) to find

$$I_{12}=\frac{r_1^2+r_2^2}{r_>}-\frac{2r_1r_2r_<}{3(r_>)^2}. \quad (A.8)$$

We can therefore write

$$\int_0^{\infty} R_{n10}(r_1)R_{n20}(r_2)R_{n30}(r_1)R_{n40}(r_2) \times I(r_1,r_2)r_1^2r_2^2dr_1dr_2 =\int_0^{\infty}\left\{\int_{r_2}^{\infty}\frac{r_2^4r_1}{3}+r_2^2r_1^3 \times R_{n10}(r_1)R_{n20}(r_2)R_{n30}(r_1)R_{n40}(r_2)dr_1\right\}dr_2 +\int_0^{\infty}\left\{\int_{r_2}^{\infty}\frac{r_2^4r_1}{3}+r_2^2r_1^3 \times R_{n10}(r_2)R_{n20}(r_1)R_{n30}(r_2)R_{n40}(r_1)dr_1\right\}dr_2. \quad (A.9)$$

The terms R_{10}, R_{20}, and R_{30} are given by

$$R_{10}=4\sqrt{2}e^{-2r},$$
$$R_{20}=2e^{-r}(1-r),$$
$$R_{30}=(4\sqrt{2}/81\sqrt{3})e^{-\frac{2}{3}r}(27-36r+8r^2). \quad (A.10)$$

The matrix element $\langle(H')^{-1}\psi_1^0,\psi_1^0\rangle$ is thus given by

$$\langle(H')^{-1}\psi_1^0,\psi_1^0\rangle =\frac{2(32)^2}{3}\int_0^{\infty}\left\{\int_{r_2}^{\infty} r_2^4r_1e^{-4r_2}e^{-4r_1}dr_1\right\}dr_2 +2(32)^2\int_0^{\infty}\left\{\int_{r_2}^{\infty} r_2^2r_1^3e^{-4r_2}e^{-4r_1}dr_1\right\}dr_2. \quad (A.11)$$

Explicit evaluation of the integrals shows that

$$\langle(H')^{-1}\psi_1^0,\psi_1^0\rangle=1.093\ 750\ 0.$$

For the third intermediate problem the elements p_i are given by

$$p_1=(r_{12}/4\pi)\{R_{10}(r_1)R_{10}(r_2)\},$$
$$p_2=(r_{12}/\sqrt{2}4\pi)\{R_{10}(r_1)R_{20}(r_2)+R_{10}(r_2)R_{20}(r_1)\}, \quad (A.12)$$
$$p_3=(r_{12}/\sqrt{2}4\pi)\{R_{10}(r_1)R_{30}(r_2)+R_{10}(r_2)R_{30}(r_1)\}.$$

In order to aid in the evaluation of the matrix elements

$$\langle p_i,\psi_j^0\rangle=\langle(H')^{-1}\psi_i^0,\psi_j^0\rangle, \quad (i,\ j=1,\ 2,\ 3), \quad (A.13)$$

a table of integrals

$$I(\alpha_1,\alpha_2,\beta_1,\beta_2) =\int_0^{\infty} r_2^{\alpha_1}e^{-\beta_1r_1}\left\{\int_{r_2}^{\infty} r_1^{\alpha_2}e^{-\beta_2r_1}dr_1\right\}dr_2, \quad (A.14)$$

was evaluated from a closed-form expression on the IBM 704. The final results for (A.13) are

$$\begin{aligned}
&\langle(H')^{-1}\psi_1^0,\psi_1^0\rangle=1.093\ 750,\\
&\langle(H')^{-1}\psi_1^0,\psi_2^0\rangle=-0.318\ 511,\\
&\langle(H')^{-1}\psi_1^0,\psi_3^0\rangle=-0.134\ 091,\\
&\langle(H')^{-1}\psi_2^0,\psi_2^0\rangle=3.085\ 264,\\
&\langle(H')^{-1}\psi_2^0,\psi_3^0\rangle=-0.909\ 351,\\
&\langle(H')^{-1}\psi_3^0,\psi_3^0\rangle=6.795\ 531.
\end{aligned} \quad (A.15)$$

ACKNOWLEDGMENTS

The author wishes to express his gratitude to L. E. Payne for his encouragement and many fruitful discussions concerning this paper. The author also thanks D. Fox, H. F. Weinberger, and A. Weinstein for their kind interest.