

Introduction to the contributions of A. Temkin and R. J. Drachman to atomic physics

A. K. Bhatia

NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

Dr. Aaron Temkin and Dr. Richard J. Drachman have made significant contributions in the field of atomic physics during nearly the last fifty years. It is not possible to enumerate all of their contributions but I will describe a few, first those of Temkin and then of Drachman. Some of the topics of their research are discussed in the articles that follow this one.

Method of Polarized Orbitals

Their work, as is the work of most atomic theorists, is concerned with solving the Schrödinger equation accurately for wave function in cases where there is no exact analytical solution. In particular, Temkin is associated with electron scattering from atoms (and ions). When he started there already were a number of methods to study the scattering of electrons from atoms. The simplest approximation for a hydrogenic target is the static approximation

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = u(\mathbf{r}_1)\Phi_{\text{target}}(\mathbf{r}_2), \quad (1)$$

where $u(\mathbf{r}_1)$ is the scattering function. This gives rise, in a partial wave expansion, to differential equations which can be solved easily. An important improvement on this approximation is the exchange approximation of Morse and Allis [1] in which the target is assumed to remain in its original state in the presence of the incident electron but the ansatz for the wave function is explicitly (anti)symmetrized

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = u(\mathbf{r}_1)\Phi_{\text{target}}(\mathbf{r}_2) \pm u(\mathbf{r}_2)\Phi_{\text{target}}(\mathbf{r}_1), \quad (2)$$

where the upper sign refers to singlet scattering and the lower sign to the triplet scattering. This gives rise to an integro-differential equation which will be given later.

But in reality, the target does not stay in its original state and various forms of polarization potentials have been added to the equation for $u(r)$ to take into account this distortion. The method of polarized orbitals proposed by Temkin [2] was the first method to include the effect of polarization in the ansatz for the total wave function. It has been used for scattering of slowly moving electrons from various targets so that the target is distorted adiabatically. This means the target is assumed to follow the instantaneous motion of the scattered electron. The basic problem is how to take into account this distortion mathematically. I will discuss it for a simple target like the hydrogen atom in its ground state (1s), following Temkin [3]. The Hamiltonian H (in Ry units) for two electrons in the field of the nucleus of charge Z is given by

$$H = -\nabla_1^2 - \nabla_2^2 - \frac{2Z}{r_1} - \frac{2Z}{r_2} + \frac{2}{r_{12}}, \quad (3)$$

which for an incoming electron 1 can be written as

$$H = H_0 + V(\mathbf{r}_1, \mathbf{r}_2), \quad (4)$$

where H_0 also contains ∇_1^2

$$H_0 = -\nabla_1^2 - \nabla_2^2 - \frac{2Z}{r_2} - \frac{2(Z-1)}{r_1}, \quad (5)$$

$$V(\mathbf{r}_1, \mathbf{r}_2) = -\frac{2}{r_1} + \frac{2}{r_{12}}, \quad (6)$$

and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. The first order perturbed wave function of the electron 2 due to the potential V can be written as

$$\Psi_{\text{pol}}(\mathbf{r}_1, \mathbf{r}_2) = \Phi_{100}(\mathbf{r}_2) - \sum'_{n,l} \frac{\langle nl0|V(\mathbf{r}_1, \mathbf{r}_2)|100\rangle}{\epsilon_n - \epsilon_1} \Phi_{nl0}(\mathbf{r}_2), \quad (7)$$

where integration over continuum states is implied and $\epsilon_n = -Z^2 n^{-2}$ is the energy of the n th hydrogenic state Φ_{nlm} which is given by

$$\Phi_{nlm}(\mathbf{r}_2) = \frac{u_{nl}(r_2)}{r_2} Y_{lm}(\Omega_2). \quad (8)$$

The perturbing potential V for $r_1 > r_2$ is given by

$$V(\mathbf{r}_1, \mathbf{r}_2) = 2 \sum_{l=1}^{\infty} \frac{r_2^l}{r_1^{l+1}} P_l(\cos\theta_2), \quad (9)$$

where we have fixed the z -axis in the direction of \mathbf{r}_1 and have used the well-known expansion of $1/r_{12}$. Noting that the $l=0$ term drops out of $V(\mathbf{r}_1, \mathbf{r}_2)$, we can write the matrix in Eq. (7) as

$$\begin{aligned} \langle nl0|V(\mathbf{r}_1, \mathbf{r}_2)|100\rangle Y_{l0}(\Omega_2) &= \left[\frac{1}{r_1^{l+1}} \int_0^{r_1} u_{nl}(r'_2) r_2'^l u_{10}(r'_2) dr'_2 \right. \\ &\quad \left. + r_1^l \int_{r_1}^{\infty} u_{nl}(r'_2) \frac{1}{r_2'^{l+1}} u_{10}(r'_2) dr'_2 \right] \frac{2}{(4\pi)^{\frac{1}{2}}} P_l(\cos\theta_2). \end{aligned} \quad (10)$$

The second integral vanishes in the limit $r_1 \rightarrow \infty$ and the above matrix for large r_1 can be approximated by

$$\langle nl0|V(\mathbf{r}_1, \mathbf{r}_2)|100\rangle Y_{l0}(\Omega_2) \cong \left[\frac{1}{r_1^{l+1}} \int_0^{\infty} u_{nl}(r'_2) r_2'^l u_{10}(r'_2) dr'_2 \right] \frac{2}{(4\pi)^{\frac{1}{2}}} P_l(\cos\theta_2), \quad (11)$$

which can be written as

$$\langle nl0|V(\mathbf{r}_1, \mathbf{r}_2)|100\rangle Y_{l0}(\Omega_2) \cong \left[\frac{1}{r_1^{l+1}} \langle nl|r_2'^l|10\rangle \right] \frac{2}{(4\pi)^{\frac{1}{2}}} P_l(\cos\theta_2). \quad (12)$$

Now Eq. (7) can be written as

$$\Psi_{\text{pol}}(\mathbf{r}_1, \mathbf{r}_2) \cong \Phi(\mathbf{r}_1, \mathbf{r}_2) = \Phi_{100} - \sum_{l=1}^{\infty} \frac{2}{r_1^{l+1}} \frac{P_l(\cos\theta_2)}{(4\pi)^{\frac{1}{2}}} \sum_{n=l+1}^{\infty} \frac{\langle nl|r_2^l|10\rangle}{\epsilon_n - \epsilon_1} \frac{u_{nl}(r_2)}{r_2}. \quad (13)$$

To sum this series, use the fact that the bound states satisfy

$$\left[-\nabla_2^2 - \frac{2Z}{r_2} \right] u_{nl}(\mathbf{r}_2) = \epsilon_n \frac{u_{nl}(r_2)}{r_2} P_l(\cos\theta_2), \quad (14)$$

and therefore

$$\left[-\nabla_2^2 - \frac{2Z}{r_2} - \epsilon_1 \right] u_{nl}(\mathbf{r}_2) = (\epsilon_n - \epsilon_1) \frac{u_{nl}(r_2)}{r_2} P_l(\cos\theta_2), \quad (15)$$

which implies (letting $\Delta\Phi \equiv \Phi_{100} - \Phi(r_1, \mathbf{r}_2)$)

$$\begin{aligned} \left[-\nabla_2^2 - \frac{2Z}{r_2} - \epsilon_1 \right] \Delta\Phi &= \sum_{l=1}^{\infty} \frac{2}{r_1^{l+1}} \sum_{n=l+1}^{\infty} \langle nl|r_2^l|10\rangle \frac{u_{nl}(r_2)}{r_2} \frac{P_l(\cos\theta_2)}{(4\pi)^{\frac{1}{2}}} \\ &= \sum_{l=1}^{\infty} \frac{2}{r_1^{l+1}} \sum_{n=l+1}^{\infty} |u_{nl}(r_2)\rangle \langle nl|r_2^l|10\rangle \frac{P_l(\cos\theta_2)}{r_2(4\pi)^{\frac{1}{2}}}. \end{aligned} \quad (16)$$

Use now completeness

$$\sum_{n=l+1}^{\infty} |u_{nl}(r_2)\rangle \langle u_{nl}(r_2)| = \delta(r_2 - r_2'), \quad (17)$$

for any l , so that $\Delta\Phi$ satisfies the differential equation

$$\left[-\nabla_2^2 - \frac{2Z}{r_2} - \epsilon_1 \right] \Delta\Phi = 2 \sum_{l=1}^{\infty} \frac{r_2^l}{r_1^{l+1}} \Phi_{100}(r_2) P_l(\cos\theta_2), \quad (18)$$

where we have used Eq. (8) for Φ_{100} . Expanding

$$\Delta\Phi = \sum_{l=1}^{\infty} \frac{u_{1s \rightarrow l}(r_2)/r_2}{r_1^{l+1}} \frac{P_l(\cos\theta_2)}{(4Z\pi)^{\frac{1}{2}}}. \quad (19)$$

reduces Eq. (18) to the set of uncoupled equations for each l

$$\left[-\frac{d^2}{dr_2^2} - \frac{2Z}{r_2} + \frac{l(l+1)}{r_2^2} - \epsilon_1 \right] u_{1s \rightarrow l}(r_2) = 2\sqrt{Z} r_2^l u_{1s}(r_2), \quad (20)$$

where $u_{1s}(r) = 2\sqrt{Z^3} r e^{-Zr}$. Eq. (20) can be solved analytically

$$u_{1s \rightarrow l}(r_2) = 2e^{-Zr_2} \left(Z \frac{r_2^{l+2}}{l+1} + \frac{r_2^{l+1}}{l} \right). \quad (21)$$

The method of polarized orbitals uses only the dipole part ($l = 1$) of $\Delta\Phi$ [4] so that the polarized part of the target is

$$\Phi_1^{\text{pol}} = \Phi_{100} - \frac{\epsilon(r_1, r_2)}{r_1^2} \frac{u_{1s \rightarrow p}(r_2)}{r_2} \frac{P_1(\cos\theta_{12})}{(4Z\pi)^{\frac{1}{2}}}, \quad (22)$$

where θ_{12} is the angle between \mathbf{r}_1 and \mathbf{r}_2 and Temkin has introduced the step function

$$\begin{aligned} \epsilon(r_1, r_2) &= 1, & r_1 > r_2 \\ &= 0, & r_1 < r_2. \end{aligned} \quad (23)$$

which ensures that polarization takes place only when the scattered electron is outside the orbital electron. The second term in Eq. (22) is called $\Phi_1^{\text{pol}}(\mathbf{r}_1, \mathbf{r}_2)$ and gives the distortion of the orbit of hydrogen atom in its ground state (1s). This then solves the problem of the inclusion of polarization in the wave function, for substituting Eq. (22) into Eq. (13) one gets the explicit form of the polarized orbital wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = u_l(\mathbf{r}_1) [\Phi_{100}(\mathbf{r}_2) + \Phi_1^{\text{pol}}(\mathbf{r}_1, \mathbf{r}_2)] \pm u_l(\mathbf{r}_2) [\Phi_{100}(\mathbf{r}_1) + \Phi_1^{\text{pol}}(\mathbf{r}_2, \mathbf{r}_1)], \quad (24)$$

where

$$u_l(\mathbf{r}) = \frac{u_l(r)}{r} Y_{l0}(\Omega) \quad (25)$$

The scattering equation is obtained from

$$\int Y_{10}^*(\Omega_1) \Phi_0^*(\mathbf{r}_2) (H - E) \Psi(\mathbf{r}_1, \mathbf{r}_2) d\Omega_1 d\mathbf{r}_2 = 0, \quad (26)$$

$$E = -Z^2 + k^2, \quad (27)$$

where H is the Hamiltonian, E is the total energy, k^2 is the energy of the incident electron and $\Phi_{100} \equiv \Phi_0$. We will derive the scattering equation for any Z , the charge of the nucleus. If the variational principle were used it would require that we operate on the left by $(\Phi_0 + \Phi_1^{\text{pol}})$. This would give us higher order terms which are not in accord with the first-order perturbation theory. (It would also give quadratic terms involving Φ_1^{pol} which would be singular if the step function $\epsilon(r_1, r_2)$ were retained in its definition.) Therefore, Temkin has multiplied on the left by Φ_0 only in Eq. (26). (In retrospect, the main disadvantage of this ansatz is the loss of any bound on the calculated phase shifts from this equation.) The resulting integro-differential equation for $u_l(r)$ [5], including the p -wave ($l=1$) correction of Sloan [6] is, letting $r_1=r$,

$$\begin{aligned} \left[\frac{d^2}{dr^2} + k^2 + v_{st}(r) - \frac{l(l+1)}{r^2} \right] u_l(r) &\pm 4Z^3 e^{-Zr} [(k^2 + Z^2) r \delta_{l0} \int_0^\infty dr_2 e^{-Zr_2} r_2 u_l(r_2) \\ &- \frac{2}{2l+1} (r^{-l} \int_0^r dr_2 e^{-Zr_2} r_2^{l+1} u_l(r_2) + r^{l+1} \int_r^\infty dr_2 \frac{e^{-Zr_2}}{r_2^l} u_l(r_2))] \end{aligned}$$

$$\begin{aligned}
 &= -\frac{\beta(Zr)}{(Zr)^4}u_l(r) \\
 &\mp 4Ze^{-Zr}\left[\frac{1}{3}\delta_{l1}\left(-\frac{1}{2}Z(Z^2+k^2)r^3+(Z^2-k^2)r^2\right)\int_r^\infty dr_2\frac{e^{-Zr_2}}{r_2^l}u_l(r_2)\right. \\
 &+ 2\left(\frac{Zr^3}{2}+r^2\right)\left(\frac{l}{(2l-1)(2l+1)}r^{l-1}\int_r^\infty dr_2\frac{e^{-Zr_2}}{r_2^{l+1}}u_l(r_2)\right. \\
 &+ \left.\left.\frac{l+1}{(2l+1)(2l+3)}r^{l+1}\int_r^\infty dr_2\frac{e^{-Zr_2}}{r_2^{l+3}}u_l(r_2)\right)\right] \\
 &\pm \frac{4}{3}Ze^{-2Zr}\delta_{l1}\left[\left(\frac{3}{2}Z^2r^2+\frac{1}{2}Zr-3\right)u_l(r)-\left(\frac{Zr^2}{2}+r\right)\frac{du_l}{dr}\right], \tag{28}
 \end{aligned}$$

where the static potential is given by

$$v_{st}(r) = 2\frac{(Z-1)}{r} + 2\left(Z + \frac{1}{r}\right)e^{-2Zr}, \tag{29}$$

and the direct polarization potential is given by

$$\beta(Zr)/(Zr)^4 \rightarrow \alpha/r^4 \quad \text{for } r \rightarrow \infty, \tag{30}$$

where

$$\beta(x) = \frac{9}{2} - \frac{2}{3}e^{-2x}(x^5 + \frac{9}{2}x^4 + 9x^3 + \frac{27}{2}x^2 + \frac{27}{2}x + \frac{27}{4}). \tag{31}$$

Note that the polarized orbital ansatz Eq. (24) provides a natural cut off for the polarization potential $\beta(Zr)/r^4 \rightarrow 0$ as $r \rightarrow 0$ and gives the correct polarizability as $r \rightarrow \infty$, where $\alpha = 9/2Z^4$ is the dipole polarizability of the target with nuclear charge Z . We get the equation for the exchange approximation [1] by putting the right hand side equal to 0 and we get exchange adiabatic approximation by retaining the first term on the right hand side which is the direct polarization potential.

Eq. (28) can be solved for the function $u_l(r)$ with the phase shifts η_l being obtained from the values of the function at large distance:

$$\lim_{r \rightarrow \infty} u_l(r) \propto \sin(kr - l\frac{\pi}{2} + \eta) \tag{32}$$

The phase shifts for electron-hydrogen scattering for S -wave and P -wave are given in Table I for various k in three different methods: exchange approximation, polarized orbital method and Kohn variation principle [7,8]. The effect of the polarization is dominated by the direct $-\alpha/r^4$ potential and always has the effect of increasing the phase shifts relative to the exchange approximation. The effect of exchange polarization terms is smaller and can be either positive or negative depending on the spin. The 1S and 3S results decrease with increasing k while 3P results increase with increasing k . The effect of the exchange polarization terms in the 1P case leads to three changes in sign of phase shift as k increases, indicating that the method does include the essential physics. This is the first method to give three changes of sign of the 1P phase shifts correctly (cf. Fig. 6-1-5 in [9]). We will return to the question of bounds in another section.

TABLE I. e-H phase shifts of 1S , 3S , 1P , and 3P for various k in different approximations.

Partial Wave	k	Exch.	PO ^a	KVP ^b	Exch.	PO ^a	KVP ^b
		Singlet			Triplet		
S	0^c	8.10	5.9	5.965	2.35	1.9	1.7686
	0.1	2.396	2.583	2.553	2.907	2.945	2.939
	0.2	1.870	2.144	2.0673	2.679	2.732	2.7171
	0.3	1.508	1.750	1.6964	2.461	2.519	2.4996
	0.4	1.239	1.469	1.4146	2.257	2.320	2.2938
	0.5	1.031	1.251	1.202	2.070	2.133	2.1046
	0.7^d	0.7415	0.947	0.930	1.748	1.815	1.7797
	0.8^d	0.6513	0.854	0.886	1.617	1.682	1.643
P	0.1	-0.0012	0.0067	0.007	0.00220	0.0109	0.0114
	0.2	-0.0084	0.0171	0.0147	0.01666	0.0486	0.0450
	0.3	-0.0240	0.0210	0.0170	0.05192	0.1151	0.1063
	0.4	-0.0461	0.0163	0.0100	0.10497	0.2005	0.1872
	0.5	-0.0703	0.0064	-0.0007	0.16935	0.2867	0.2705
	0.6	-0.0919	-0.0039	-0.009	0.23183	0.3574	0.3412
	0.7	-0.1077	-0.0100	-0.013	0.28329	0.4063	0.3927
	0.8	-0.1154	-0.0095	-0.004 ^e	0.32044	0.4351	0.427
	0.9	-0.1146	-0.0015		0.34436	0.4487	
	1.0	-0.1058	0.0135		0.35791	0.4520	

^a S -wave phase shifts obtained by Temkin and Lamkin [5] using the method of polarized orbital. The P -wave results are from Sloan [6].

^b Kohn variational results for S -wave are from Schwartz [7] and P -wave results are from Armstead [8].

^c The $k=0$ entries are scattering lengths [5].

^d The polarized orbital results are from [9].

^e Beyond $k=0.8$ the phase shift becomes positive and in fact goes through a (1P) resonance at $k=0.846$

On the other hand, scattering length a , which is defined as

$$\lim_{k \rightarrow 0} k \cot \eta = -1/a, \quad (33)$$

does have an upper bound, in the variational calculation [7] $a_{\text{exact}} \leq a_{\text{calculated}}$. The scattering lengths in various approximations are given in Table I. For the triplet state, Rosenberg *et al.* [10] had obtained $a_t \leq 1.91$ for the electron-hydrogen scattering. They used an s -wave function having a correct asymptotic form at infinity but did not have a slowly vanishing part ($\frac{1}{r^2}$), as subsequently pointed out by Temkin [11]. Furthermore, Temkin [11] showed that the expression for the scattering length calculated at a finite distance R should be corrected

$$a = a(R) - \alpha \left(\frac{1}{R} - \frac{a}{R^2} + \frac{1}{3} \frac{a^2}{R^3} \right), \quad (34)$$

where a is the true scattering length, and α the polarizability of the target. With this modification Temkin obtained an improved value

$$a_t = 1.74, \quad (35)$$

compared to the previous value of 1.91 [5] given in the Table I. After the publication of Temkin's formula (34) and his numerical result in Eq. (35), Schwartz [7] did use such a slowly vanishing part $1/r^2$ in his trial wave function, obtaining precision results:

$$a_s = 5.965 \pm 0.0003 \quad \text{and} \quad a_t = 1.7686 \pm 0.0002, \quad (36)$$

for the singlet (*s*) and triplet (*t*) scattering lengths.

Symmetric Euler-Angle Decomposition

In most of the scattering and eigenvalue problems, it is necessary to write the required wave function in terms of a product of two components: radial and angular. Only then the Hamiltonian operating on such a wave function gives equations which depend on the internal coordinates only, with terms arising from the operation of the angular part contained in the Hamiltonian. For one particle scattering from a fixed center, (or the relative motion of two particles) the Laplacian operator is of the form

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) + \frac{1}{r^2} \left(\frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} \right), \quad (37)$$

where the radial and angular parts can be separated and the second term is proportional to the square of the angular momentum operator. When acting on a wave function which is an eigenfunction of angular momentum l , the Laplacian simplifies to

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial}{\partial r}) - \frac{l(l+1)}{r^2}, \quad (38)$$

thus converting a 3-dimensional partial differential equation into an ordinary differential equation.

In the case of two particles in an external force field, e.g., the field of the fixed nucleus (i.e., of infinite mass), the decomposition of the Laplacians is not as simple as in the case of relative motion of two particles. The wave function describing these particles is a function of the internal (i.e., meaning coordinates depending on the position of the nucleus and on two electrons in a plane) coordinates (r_1, r_2, θ_{12}) or (r_1, r_2, r_{12}) and the angular component which is a function of three Euler angles which describe the orientation of the instantaneous plane formed by the two particles and the nucleus in space. The Euler angles are not unique. Breit [12] used the Euler angles which Hylleraas [13] introduced. These are two spherical angles of one the particles and the angle between the $r_1 - z$ plane and $r_1 - r_2$ plane, the internal coordinates being (r_1, r_2, θ_{12}) . Breit introduced these angles for *P*-wave functions and - because they are not symmetrically defined with respect to the two electrons - it is not easy to generalize this decomposition for all angular momenta. Temkin introduced a different set of symmetric Euler angles which allowed the separation of the radial part and angular part for any angular momentum l . The analysis of this problem was carried out by Bhatia and Temkin [14]. Fig. 1 contains a perspective drawing of the Euler angles which define the particle plane with respect to the space fixed x , y , and z axes.

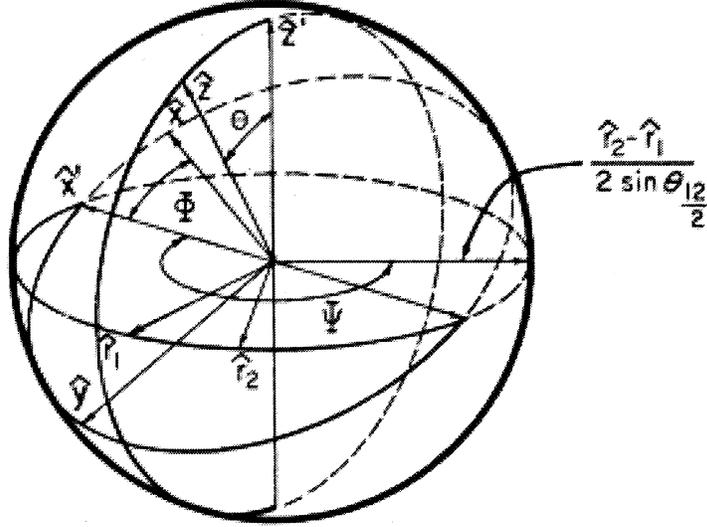


Figure 1: Perspective drawing of the Euler angles the unit vector of the problem.

The rotated axes x', y', z' with respect to the space fixed axes x, y, z are defined by

$$\hat{z}' = \frac{\hat{r}_1 \times \hat{r}_2}{|\hat{r}_1 \times \hat{r}_2|}. \quad (39)$$

Having defined \hat{z}' , define \hat{x}'

$$\hat{x}' = \frac{\hat{z} \times \hat{z}'}{|\hat{z} \times \hat{z}'|}. \quad (40)$$

Having defined \hat{z}' and \hat{x}' , define \hat{y}'

$$\hat{y}' = \hat{z}' \times \hat{x}'. \quad (41)$$

The Euler angles are then

$$\Theta \equiv \text{angle between } \hat{z} \text{ and } \hat{z}', \quad (42)$$

$$\Phi \equiv \text{angle between } \hat{x}' \text{ and } \hat{x}, \quad (43)$$

$$\Psi \equiv \text{angle between } \hat{x}' \text{ and } (\hat{r}_2 - \hat{r}_1). \quad (44)$$

The operation of parity ($\mathbf{r}_1 \rightarrow -\mathbf{r}_1$ and $\mathbf{r}_2 \rightarrow -\mathbf{r}_2$) only involves the Euler angles

$$\begin{aligned} \Theta &\rightarrow \Theta, \\ \Phi &\rightarrow \Phi, \\ \Psi &\rightarrow \pi + \Psi. \end{aligned} \quad (45)$$

Exchange corresponds to the transformation $\mathbf{r}_1 \Leftrightarrow \mathbf{r}_2$ and is given by $r_1 \Leftrightarrow r_2$ plus the following transformation of the Euler angles

$$\begin{aligned}\Theta &\rightarrow \pi - \Theta, \\ \Phi &\rightarrow \pi + \Phi, \\ \Psi &\rightarrow 2\pi - \Psi.\end{aligned}\tag{46}$$

The eigenfunctions of total angular momentum are purely functions of the Euler angles. Temkin has coined the name "rotational harmonics" for these eigenfunctions (they are usually called \mathcal{D} functions). The angular momentum properties of these functions are

$$\mathbf{M}^2 \mathcal{D}_l^{m,k} = \hbar l(l+1) \mathcal{D}_l^{m,k},\tag{47}$$

and

$$M_z \mathcal{D}_l^{m,k} = \hbar m \mathcal{D}_l^{m,k}.\tag{48}$$

They transform under parity as

$$\mathcal{P} \mathcal{D}_l^{m,k}(\Theta, \Phi, \Psi) \equiv \mathcal{D}_l^{m,k}(\Theta, \Phi, \pi + \Psi) = (-1)^k \mathcal{D}_l^{m,k}(\Theta, \Phi, \Psi),\tag{49}$$

and exchange as

$$\mathcal{E}_{12} \mathcal{D}_l^{m,k}(\Theta, \Phi, \Psi) \equiv \mathcal{D}_l^{m,k}(\pi - \Theta, \pi + \Phi, 2\pi - \Psi) = (-1)^l \mathcal{D}_l^{m,-k}(\Theta, \Phi, \Psi).\tag{50}$$

We see that whereas the \mathcal{D} functions are eigenfunctions of parity, that they actually change indices under \mathcal{E}_{12} . But operation of exchange commutes with the total Hamiltonian, therefore it must be possible to construct eigenfunctions of exchange: they are linear combinations of the above \mathcal{D} functions. For $m=0$ they are

$$\mathcal{D}_l^{\kappa+} = \frac{\mathcal{D}_l^{0,\kappa} + (-1)^\kappa \mathcal{D}_l^{0,-\kappa}}{\sqrt{2}[1 + \delta_{0\kappa}(\sqrt{2} - 1)]},\tag{51}$$

and

$$\mathcal{D}_l^{\kappa-} = \frac{\mathcal{D}_l^{0,\kappa} - (-1)^\kappa \mathcal{D}_l^{0,-\kappa}}{i\sqrt{2}}.\tag{52}$$

Under exchange these linear combinations have the property

$$\mathcal{E}_{12} \mathcal{D}_l^{\kappa\pm} = \pm (-1)^{l+\kappa} \mathcal{D}_l^{\kappa\pm}.\tag{53}$$

Thus they are indeed eigenfunctions of exchange. Having constructed eigenfunctions (of the angular part) of exchange, one can construct a total wave function which has the correct properties under operations of parity and full exchange

$$\Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\kappa}'' [f_l^{\kappa+}(r_1, r_2, \theta_{12}) \mathcal{D}_l^{\kappa+}(\Theta, \Phi, \Psi) + f_l^{\kappa-}(r_1, r_2, \theta_{12}) \mathcal{D}_l^{\kappa-}(\Theta, \Phi, \Psi)], \quad (54)$$

where the double prime on the summation indicates that the sum goes over every second value of κ . The operation under exchange on Eq. (54) gives,

$$\begin{aligned} \mathcal{E}_{12}\Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{l0}(\mathbf{r}_2, \mathbf{r}_1) &= \sum_{\kappa}'' [f_l^{\kappa+}(r_2, r_1, \theta_{12}) (-1)^{l+\kappa} \mathcal{D}_l^{\kappa+}(\Theta, \Phi, \Psi) \\ &+ f_l^{\kappa-}(r_2, r_1, \theta_{12}) (-1)^{l+\kappa+1} \mathcal{D}_l^{\kappa-}(\Theta, \Phi, \Psi)]. \end{aligned} \quad (55)$$

If therefore

$$f_l^{\kappa+}(r_2, r_1, \theta_{12}) = \pm (-1)^{l+\kappa} f_l^{\kappa+}(r_1, r_2, \theta_{12}), \quad (56)$$

and

$$f_l^{\kappa-}(r_2, r_1, \theta_{12}) = \pm (-1)^{l+\kappa+1} f_l^{\kappa-}(r_1, r_2, \theta_{12}), \quad (57)$$

then under complete exchange

$$\mathcal{E}_{12}\Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2) \equiv \Psi_{l0}(\mathbf{r}_2, \mathbf{r}_1) = \pm \Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2), \quad (58)$$

i.e., the total wave function will be symmetric (singlet) or antisymmetric (triplet). Under parity we see from Eq. (54) that

$$\mathcal{P}\Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2) = \Psi_{l0}(-\mathbf{r}_1, -\mathbf{r}_2) = (-1)^{\kappa} \Psi_{l0}(\mathbf{r}_1, \mathbf{r}_2), \quad (59)$$

so that parity is determined by evenness or oddness of κ in Eq. (54).

The kinetic energy part is given by

$$\begin{aligned} \nabla_1^2 + \nabla_2^2 &= \frac{1}{r_1} \frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2} \frac{\partial^2}{\partial r_2^2} r_2 + \frac{1}{r_1^2} \left(\frac{1}{\sin\theta_1} \frac{\partial}{\partial\theta_1} \sin\theta_1 \frac{\partial}{\partial\theta_1} + \frac{1}{\sin^2\theta_1} \frac{\partial^2}{\partial\phi_1^2} \right) \\ &+ \frac{1}{r_2^2} \left(\frac{1}{\sin\theta_2} \frac{\partial}{\partial\theta_2} \sin\theta_2 \frac{\partial}{\partial\theta_2} + \frac{1}{\sin^2\theta_2} \frac{\partial^2}{\partial\phi_2^2} \right). \end{aligned} \quad (60)$$

Historically, this was the extent of the development when I came to work with Dr. Temkin in 1963. I worked for almost a year to convert the kinetic energy into Euler angles (plus internal coordinates) form. The following is the result

$$\nabla_1^2 + \nabla_2^2 = \frac{1}{r_1} \frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2} \frac{\partial^2}{\partial r_2^2} r_2 + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \left(\frac{1}{\sin\theta_{12}} \frac{\partial}{\partial\theta_{12}} \sin\theta_{12} \frac{\partial}{\partial\theta_{12}} \right) + \frac{F_1}{r_1^2} + \frac{F_2}{r_2^2} \quad (61)$$

$$\begin{aligned}
 F_1 = & \frac{1}{\sin^2\theta_{12}} \left[\sin^2(\Psi + \frac{1}{2}\theta_{12}) \frac{\partial^2}{\partial\Theta^2} + \cos^2(\Psi + \frac{1}{2}\theta_{12}) \cot\Theta \frac{\partial}{\partial\Theta} \right. \\
 & + \cos^2(\Psi + \frac{1}{2}\theta_{12}) \frac{1}{\sin^2\Theta} \frac{\partial^2}{\partial\Phi^2} + \sin(2\Psi + \theta_{12}) \frac{\cot\Theta}{\sin\Theta} \frac{\partial}{\partial\Phi} \\
 & - \sin(2\Psi + \theta_{12}) \frac{1}{\sin\Theta} \frac{\partial^2}{\partial\Theta\partial\Phi} + \sin(2\Psi + \theta_{12}) \cot\Theta \frac{\partial^2}{\partial\Psi\partial\Theta} \\
 & \left. - 2\cos^2(\Psi + \frac{1}{2}\theta_{12}) \frac{\cot\Theta}{\sin\Theta} \frac{\partial^2}{\partial\Psi\partial\Phi} \right] - \frac{\partial^2}{\partial\Psi\partial\theta_{12}} + A_1 \frac{\partial^2}{\partial\Psi^2} + B_1 \frac{\partial}{\partial\Psi}
 \end{aligned} \quad (62)$$

$$A_1 = \frac{1}{4} + (\cot^2\Theta/\sin^2\theta_{12})\cos^2(\Psi + \frac{1}{2}\theta_{12}) \quad (63)$$

$$B_1 = (\cos\Psi/\sin^2\theta_{12})\sin(\Psi + \theta_{12}) - [\sin(2\Psi + \theta_{12})/\sin^2\theta_{12}\sin^2\Theta] - \frac{1}{2}\cot(\frac{1}{2}\theta_{12}). \quad (64)$$

The expressions for F_2 , A_2 , and B_2 can be obtained by replacing θ_{12} by $-\theta_{12}$ in the above expressions for F_1 , A_1 , and B_1 .

With these results the Schrödinger equation

$$H\Psi_{lm} = E\Psi_{lm} \quad (65)$$

for any m , can be reduced to radial equations which are independent of m :

$$\begin{aligned}
 [L_{\theta_{12}} + \frac{2m_e}{\hbar^2}(E - V)]f_l^{\kappa+} - (\frac{1}{r_1^2} + \frac{1}{r_2^2}) \left[\left\{ \frac{l(l+1) - \kappa^2}{2\sin^2\theta_{12}} + \frac{\kappa^2}{4} - \frac{\cot\theta_{12}}{4\sin\theta_{12}} l(l+1)\delta_{1\kappa} \right\} f_l^{\kappa+} \right. \\
 + \frac{\cot\theta_{12}}{4\sin\theta_{12}} B_l^{\kappa+2} f_l^{(\kappa+2)+} + \frac{\cot\theta_{12}}{4\sin\theta_{12}} (1 - \delta_{0\kappa} - \delta_{1\kappa} + \delta_{2\kappa}) B_{l\kappa} f_l^{(\kappa-2)+}] \\
 + (\frac{1}{r_1^2} - \frac{1}{r_2^2}) \left[-\kappa \left(\frac{1}{2}\cot\theta_{12} + \frac{\partial}{\partial\theta_{12}} \right) f_l^{\kappa-} - \frac{l(l+1)}{4\sin\theta_{12}} \delta_{1\kappa} f_l^{\kappa-} \right. \\
 \left. + \frac{B_l^{\kappa+2}}{4\sin\theta_{12}} f_l^{(\kappa+2)-} - \frac{1}{4\sin\theta_{12}} (1 - \delta_{0\kappa} - \delta_{1\kappa} - \delta_{2\kappa}) B_{l\kappa} f_l^{(\kappa-2)-} \right] = 0
 \end{aligned} \quad (66)$$

and

$$\begin{aligned}
 [L_{\theta_{12}} + \frac{2m_e}{\hbar^2}(E - V)]f_l^{\kappa-} - (\frac{1}{r_1^2} + \frac{1}{r_2^2}) \left[\left\{ \frac{l(l+1) - \kappa^2}{2\sin^2\theta_{12}} + \frac{\kappa^2}{4} + \frac{\cot\theta_{12}}{4\sin\theta_{12}} l(l+1)\delta_{1\kappa} \right\} f_l^{\kappa-} \right. \\
 + \frac{\cot\theta_{12}}{4\sin\theta_{12}} (1 - \delta_{0\kappa}) B_l^{\kappa+2} f_l^{(\kappa+2)-} + \frac{\cot\theta_{12}}{4\sin\theta_{12}} (1 - \delta_{0\kappa} - \delta_{1\kappa} - \delta_{2\kappa}) B_{l\kappa} f_l^{(\kappa-2)-}] \\
 + (\frac{1}{r_1^2} - \frac{1}{r_2^2}) \left[\kappa \left(\frac{1}{2}\cot\theta_{12} + \frac{\partial}{\partial\theta_{12}} \right) f_l^{\kappa+} - \frac{l(l+1)}{4\sin\theta_{12}} \delta_{1\kappa} f_l^{\kappa+} \right. \\
 \left. - \frac{(1 - \delta_{0\kappa})}{4\sin\theta_{12}} B_l^{\kappa+2} f_l^{(\kappa+2)+} + \frac{1}{4\sin\theta_{12}} (1 - \delta_{0\kappa} - \delta_{1\kappa} + \delta_{2\kappa}) B_{l\kappa} f_l^{(\kappa-2)+} \right] = 0
 \end{aligned} \quad (67)$$

where $L_{\theta_{12}}$ is the S -wave part of the kinetic energy, and is the only term which survives in the description of S -waves

$$L_{\theta_{12}} = \frac{1}{r_1} \frac{\partial^2}{\partial r_1^2} r_1 + \frac{1}{r_2} \frac{\partial^2}{\partial r_2^2} r_2 + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin \theta_{12}} \frac{\partial}{\partial \theta_{12}} \left(\sin \theta_{12} \frac{\partial}{\partial \theta_{12}} \right), \quad (68)$$

and

$$B_{l\kappa} = \frac{[(l - \kappa + 1)(l - \kappa + 2)(l + \kappa)(l + \kappa - 1)]^{\frac{1}{2}}}{[1 + \delta_{2\kappa}(\sqrt{2} - 1)]} \quad (69)$$

$$B_l^\kappa = B_{l\kappa} [1 + \delta_{2\kappa}(\sqrt{2} - 1)]^2. \quad (70)$$

The above equations can be written in terms of (r_1, r_2, r_{12}) [14]. These equations have been generalized to the case when the nucleus is of finite mass [15], and also to the case when all the particles are of unequal masses [15].

The equation given by Breit [12] for P -wave can be obtained from our equations by noting the relation between his angles and our Euler angles (cf. Appendix of our paper [14]).

I believe this analysis is one of the major mathematical achievements of Dr. Temkin and I am happy to have been a part of it. And this laid the mathematical foundation of much of our future research, also with Dr. Drachman.

Optical Potential Approach for Scattering

We follow here the Feshbach projection operator formalism [16] to obtain equations for the scattering function giving phase shifts in the elastic region. The phase shifts obtained have property of having a rigorous lower bounds.

In this formalism, in order to project out the ground state we use symmetric projection operators P and Q , which for the hydrogenic (i.e., one-electron) target can be written explicitly [17]

$$P = P_1 + P_2 - P_1 P_2, \quad (71)$$

and

$$Q = 1 - P, \quad (72)$$

which implies that $P+Q=1$ and where the spatial projectors are such that for any arbitrary function $\Phi_L(\mathbf{r}_1, \mathbf{r}_2)$

$$P_1 \Phi_L(\mathbf{r}_1, \mathbf{r}_2) = \phi_0(\mathbf{r}_1) \int \phi_0(\mathbf{r}'_1) \Phi_L(\mathbf{r}'_1, \mathbf{r}_2) d\mathbf{r}'_1. \quad (73)$$

Note, P_1 and P_2 commute with each other and are each idempotent, hence the complete P and Q operators are idempotent ($P^2=P$; $Q^2=Q$) and orthogonal ($PQ=0$). In the lim $r \rightarrow \infty$,

$$P\Psi_L \rightarrow \sin(kr - L\frac{\pi}{2} + \eta_L), \quad (74)$$

therefore $P\Psi_L$ represents a scattering function, and

$$Q\Psi_L \rightarrow 0. \quad (75)$$

Effectively $Q\Psi_L$ describes the short range part of the total wave function of the system Ψ_L . The Schrödinger equation is reduced, via an analysis which by now is well known [16], to an equation for $P\Psi_L$.

$$[PHP + \frac{PHQ \gg QHP}{E - QHQ} - E]P\Psi_L = 0 \quad (76)$$

The middle term in Eq. (76) is the formal, but well defined expression for the optical potential \mathcal{V}_{op} .

The total spatial function for the e-H and e-He⁺ for the L th partial wave is written as

$$\Psi_L(\mathbf{r}_1, \mathbf{r}_2) = \frac{u_L(r_1)}{r_1} Y_{L0}(\hat{r}_1) \phi_0(\mathbf{r}_2) \pm (1 \leftrightarrow 2) + \Phi_L(\mathbf{r}_1, \mathbf{r}_2), \quad (77)$$

and

$$P\Psi_L = \Psi_L - \Phi_L, \quad (78)$$

where the target function is given by

$$\phi_0(\mathbf{r}_2) = \sqrt{\frac{Z^3}{\pi}} \exp(-Zr_2). \quad (79)$$

The upper and lower signs correspond to singlet and triplet states, respectively. The first two terms containing u_L explicitly give rise to the exchange approximation [1] and the function Φ_L is the correlation function. For arbitrary L this function is most efficiently written in terms of the symmetric Euler angles [14]: Φ_L has exactly the form of Ψ_L in Eq. (54), whereas here the open channel part is added explicitly in Eq. (77).

The f 's we here take as functions of r_1 , r_2 , and r_{12} . The $u_L(r_1)$ of the scattered electron in Eq. (77) is determined by projecting on $\langle Y_{L0}(\Omega_1) \phi_0(\mathbf{r}_2) \rangle$:

$$\int \left[Y_{L0}(\Omega_1) \phi_0(\mathbf{r}_2) \left(PHP + \frac{PHQ \gg QHP}{E - QHQ} - E \right) P\Psi_L \right] d\Omega_1 d\mathbf{r}_2 = 0, \quad (80)$$

Carrying out the integration leads to an integro-differential equation for the scattering function $u_L(r_1)$ and letting $r_1=r$,

$$\left[\frac{d^2}{dr^2} - \frac{L(L+1)}{r^2} + v_{st}(r) \pm V_{ex} - \mathcal{V}_{op} + k^2 \right] u_L = 0, \quad (81)$$

where $v_{st}(r)$ is the direct potential [Eq. (29)] and V_{ex} is the non-local exchange potential of the "exchange approximation" [1] (cf. Eq. (28)). It should be noted that the many-body problem has

been reduced to one-body problem and the Eq. (81) can be solved for u_L easily. The integral of the optical potential acting on $u_L(r)$ is:

$$\mathcal{V}_{op}u_L = r \left\langle Y_{L0}\phi_0 PHQ \frac{1}{E - QHQ} QHP\Psi_L \right\rangle. \quad (82)$$

The optical potential is expanded in terms of the eigenspectrum of the QHQ problem:

$$\delta \left[\frac{\langle \Phi_L^* QHQ \Phi_L \rangle}{\langle \Phi_L^* Q \Phi_L \rangle} \right] = 0. \quad (83)$$

This leads to eigenfunctions $\Phi_L^{(s)}$ and eigenvalues \mathcal{E}_s . By inserting a complete set of the functions obtained from the above equation into Eq. (82), $\mathcal{V}_{op}u_L$ can be written as

$$\mathcal{V}_{op}u_L(r_1) = r_1 \sum_s^{N\omega} \frac{\langle Y_{L0}(\hat{r}_1)\phi_0(r_2) \frac{2}{r_{12}} Q \Phi_L^{(s)} \rangle \langle Q \Phi_L^{(s)} \frac{2}{r_{12}} P \Psi_L \rangle}{E - \mathcal{E}_s}. \quad (84)$$

TABLE II. e-H phase shifts of 1S , 3S , 1P , and 3P states for various k obtained from the method of polarized orbitals and from the optical potential approach.

Partial Wave	k	PO ^a	OP ^b	PO ^a	OP ^b
		Singlet		Triplet	
<i>S</i>	0.1	2.583	2.55358	2.945	2.93853
	0.2	2.144	2.06678	2.732	2.71741
	0.3	1.750	1.69816	2.519	2.49975
	0.4	1.469	1.41540	2.320	2.29408
	0.5	1.251	1.20094	2.133	2.10454
	0.6		1.04083		1.93272
	0.7 ^c	0.947	0.93111	1.815	1.77950
	0.8 ^c	0.854	0.88718	1.682	1.64379
<i>P</i>	0.1	0.0067	0.0063083	0.0109	0.010382
	0.2	0.0171	0.014988	0.0486	0.045345
	0.3	0.0210	0.016613	0.1151	0.10679
	0.4	0.0163	0.099980	0.2005	0.18730
	0.5	0.0064	-0.00084017	0.2867	0.27058
	0.6	-0.0039	-0.010359	0.3574	0.34128
	0.7	-0.0100	-0.013483	0.4063	0.39257
	0.8	-0.0095	-0.0048524	0.4351	0.42730

^a *S*-wave phase shifts obtained by Temkin and Lamkin [5] using the method of polarized orbital. The *P*-wave results are from Sloan [6].

^b Phase shifts obtained from the optical potential approach. *S*-wave results are from Ref. [19] and *P*-wave results are from Ref. [20].

^cThe polarized orbital results are from [9].

For S -wave (i.e., $L=0$), $\mathcal{D}_L=\text{constant}$ and the correlation function is only a function of the radial coordinates. The formalism up to this point had already been developed. The innovation which Dr. Temkin and I introduced was the use of a correlated function of Hylleraas form

$$\Phi_{L=0} = e^{-\gamma r_1 - \delta r_2} \sum_{lmn}^{N_\omega} C_{lmn} r_1^l r_2^m r_{12}^n \pm (1 \rightleftharpoons 2). \quad (85)$$

In particular the projection of P_1 on Φ_{L0} requires a nontrivial analytical integration [18]. Here the sum includes all triples such that $l+m+n=\omega$ and $\omega=0, 1, 2, \dots, 7, 8, 9$. The number of terms for each ω depends on spin and whether $\gamma=\delta$ or not. For P -wave (i.e., $L=1$) the correlation functions $f_L^{\kappa\pm}$ are also taken of the Hylleraas form.

To summarize the calculations, the QHQ problem is solved (for a given L , γ and δ and N_ω). The result is a set of eigenvalues \mathcal{E}_s ($s=1, 2, \dots, N_\omega$) and associated eigenfunctions $\Phi^{(s)}$. From them the optical potential, Eq. (82) is constructed, and the integro-differential Eq. (81) is solved noniteratively. The solution is unique (up to an arbitrary normalization) with asymptotic form

$$\lim_{r \rightarrow \infty} u_L(r) \propto \sin(kr - L\frac{\pi}{2} + \frac{Z-1}{k} \ln(2kr) + \arg[\Gamma(1 - \frac{i(Z-1)}{k})] + \eta_L). \quad (86)$$

Electron-hydrogen phase shifts (i.e., $Z=1$) are given in Table II. For 1S -wave scattering, the optical potential (OP) phase shifts converged to the accuracy shown when the maximum number of terms in the wave function was 95 and in 3S -wave the convergence was obtained when the number of terms was 84. The P -wave phase shifts converge slowly compared to the S -wave results. Therefore, the computation was carried up to 220 terms. The convergence [19, 20] of results suggest that they are accurate up to five significant figures after the decimal and to that accuracy they are rigorous lower bounds, provided the total energy of the system is less than those of all the resonance positions [21]. Phase shifts are compared in Table II to the polarized orbital results of Temkin and Lamkin [5] for S -wave, for P -wave with those of Sloan [6], including the exchange polarization terms. The polarized orbital method does not provide any bound on the phase shifts but they are seen to contain the dominant part of the correlation enhancement over the exchange approximation. In particular the polarized orbital 1P results show the correct undulations (as a function of k) as the precision results.

A similar calculation has been carried out for the scattering of electrons from helium ions [22, 23]. The non-Coulomb part of the phase shifts as a function of k are given in Tables III for 1S , 3S , 1P and 3P . In this case because the Coulomb field extends very far, Eq. (81) has to be integrated to large distance especially for small values of k .

In the singlet P case, the exchange approximation results are negative and there is a lot of cancellation with the contributions to the phase shifts from the optical potential, unlike in the triplet case where the exchange approximation results are always positive.

TABLE III. e-He⁺ phase shifts of ¹S, ³S, ¹P, and ³P states for various *k* obtained from the method of polarized orbitals and from the optical potential approach.

Partial Wave	<i>k</i>	Exch	PO ^a	OP ^b	Exch.	PO ^a	OP ^b	
		Singlet			Triplet			
<i>S</i>	0.4		0.4301	0.42601		0.9235	0.91300	
	0.5			0.41964			0.90275	
	0.6		0.4153	0.41278		0.9015	0.89050	
	0.7	0.34871		0.40561			0.87640	
	0.8	0.33949	0.3986	0.39857	0.85195	0.8723	0.86069	
	0.9	0.33100		0.39202	0.83444		0.84356	
	1.0	0.32302	0.3823	0.38634	0.81645	0.8371	0.82531	
	1.1	0.31577		0.38187	0.79764		0.80625	
	1.2	0.30940	0.3685	0.37899	0.77821	0.7984	0.78666	
	1.3	0.30400		0.37832	0.75851		0.76684	
	1.4	0.29957	0.3579	0.38560	0.73872	0.7591	0.74697	
	<i>P</i>	0.1	-0.070322		-0.038311	0.17705		0.21516
		0.2	-0.074161	-0.0404	-0.038958	0.17913	0.2232	0.21681
		0.3	-0.075219		-0.039911	0.18238		0.21944
0.4		-0.076473	-0.0428	-0.040971	0.18653	0.2290	0.22283	
0.5		-0.077742		-0.041951	0.19123		0.22661	
0.6		-0.078820	-0.0450	-0.042633	0.19615	0.2364	0.23048	
0.7		-0.079501		-0.042834	0.20096		0.23415	
0.8		-0.079626	-0.0457	-0.042383	0.20540	0.2429	0.23744	
0.9		-0.079078		-0.041158	0.20927		0.24008	
1.0		-0.077762	-0.0436	-0.039036	0.21245	0.2469	0.24202	
1.1		-0.075639		-0.035948	0.21489		0.24322	
1.2		-0.072707	-0.0384	-0.031838	0.21659	0.2479	0.24378	
1.3		-0.068996		-0.026592	0.21757		0.24370	
1.4		-0.064574	-0.0301	-0.019982	0.21790	0.2317	0.24320	

^a*S*-wave and *P*-wave phase shifts obtained by Sloan [6] using the method of polarized orbital.

^b Phase shifts obtained from the optical potential approach: *S*-wave results are from Ref. [22] and *P*-wave results are from Ref. [23].

Resonances in Two-Electron Systems

In the above section, projection operators *P* and *Q* for one-electron targets were given. These have been used to calculate resonance parameters for a number of ^{1,3}*S*, ^{1,3}*P*, and ^{1,3}*D* states in H⁻ and He. Unlike other methods where one has to hunt for resonance positions, they are obtained by optimizing the functional $\langle \Phi Q H Q \Phi \rangle / \langle \Phi Q \Phi \rangle$ by using the Rayleigh-Ritz variation principle. The positions obtained do not include the shift due to their being embedded in the continuum [17] and this shift is calculated separately using various approximations for the continuum functions. For illustration, only two sets of results (positions and widths) are given in Table IV for ¹*S* in H⁻

Table IV. Some results for resonance states in H^- and He

State	Position(eV)	Width(eV)	Position(eV)	Width(eV)
$^1S(H^-)$	9.55735 ± 0.00005^a	0.0004717 ± 0.00002	9.558 ± 0.010^b	
$^1P(He)$	60.133 ± 0.015^c	0.038 ± 0.004	60.151 ± 0.010^d	0.038 ± 0.002^d

^aResonance position is with respect to the ground state of H atom [24]

^bExperimental result are from Sanche and Burrow [27].

^cResonance position is with respect to the ground state of He atom [25].

^dExperimental results are from Morgan and Ederer [28].

[24] and 1P states in He [25]. This odd-parity resonance is the lowest one in the series of resonances observed in vacuum ultraviolet absorption by Madden and Codling [26].

We see that results have been calculated with high precision and they agree with the experimental results. The line shape parameter $q = -2.80 \pm 0.025$ which we have precisely defined and calculated by further manipulation of the Feshbach theory [25] also agrees very well with the experimental result -2.55 ± 0.16 [28].

Projection Operators for More Than Two-electron Systems

For targets with more than one electron, it is difficult to construct projection operators which are idempotent, i.e., $P^2 = P$ and $Q^2 = Q$. One of the difficulties is that target wave functions for more than one-electron targets cannot be written down exactly. But we can construct them in such a way that the matrix elements $\langle \Phi_m Q^2 \Phi_n \rangle = \langle \Phi_m Q \Phi_n \rangle$ for any arbitrary antisymmetric wave functions Φ_m and Φ_n . One of our motivations was to study 2S resonance below the 3S (elastic region) of the helium atom.

In order to include all coordinates explicitly, we assume LS (i.e., Russel-Saunders) coupling and introduce channel functions in such a way that the ground state ϕ_0 is coupled to the angular momentum l_i and spin $\frac{1}{2}$ of partial wave of the incoming electron

$$\psi_0(r^{(i)}) = \sum (L_0 l_i M_0 m_i | LM) (S_0 \frac{1}{2} M_{S_0} m_s | SM_S) \phi_0(x^{(i)}) Y_{l_i m_i}(\Omega_i) \chi_{\frac{1}{2} m_s}(i). \quad (87)$$

In Eq. (87) $x^{(i)}$ (both space and spin) indicates the *absence* of the i th coordinates from the total $(N+1)$ coordinates in the electron-target system. The $x^{(i)}$ signifies

$$x^{(i)} = (x_{i+1}, x_{i+2}, \dots, x_{N+1}, x_1, x_2, \dots, x_{i-1}). \quad (88)$$

Eq. (88) implies that the target has N electrons and $r^{(i)}$ in Eq. (87) implies the absence of r_i

$$r^{(i)} = (\Omega_i, s_i; x^{(i)}). \quad (89)$$

Let p_i represent a cyclic permutation, so that

$$(-1)^{p_i} = \text{parity of the permutation which carries } [1, 2, \dots, N+1] \text{ into } [i, i+1, \dots, i-1]. \quad (90)$$

Specifically $(-1)^{p_i}=1$ for $(N+1)=\text{odd}$, $(-1)^{p_i}=(-1)^{i-1}$ for $(N+1)=\text{even}$, and $(-1)^{p_1}=1$ for all N .

Following Feshbach [16], we can define the $P\Psi_l$ part of the total wave function as

$$P\Psi_l = \sum_{i=1}^{N+1} (-1)^{p_i} u_l(r_i) \psi_0(r^{(i)}). \quad (91)$$

Here $u_l(r_i)$ are scattering functions which have not been specified but have the asymptotic property for $r_i \rightarrow \infty$

$$\lim_{r_i \rightarrow \infty} u_l(r_i) = \frac{\sin(kr_i - l\pi/2 + \eta_l)}{kr_i}, \quad (92)$$

which implies that both $P\Psi$ and Ψ have the same asymptotic form

$$\lim_{r_i \rightarrow \infty} P\Psi = \lim_{r_i \rightarrow \infty} \Psi = (-1)^{p_i} \frac{\sin(kr_i - l\pi/2 + \eta_l)}{kr_i} \psi_0(r^{(i)}). \quad (93)$$

To derive a specific form of P (and Q) we also require that $Q\Psi$ have no ground state in it for any coordinate of the scattered r_i (not only as $r_i \rightarrow \infty$)

$$\langle \psi_0(r^{(i)})(1-P)\Psi \rangle = 0, \quad (94)$$

which for the purpose of the derivation can be written

$$\langle \psi_0(r^{(i)})\Psi \rangle = \langle \psi_0(r^{(i)})P\Psi \rangle. \quad (95)$$

Define the left hand side as

$$w(r_i) \equiv (-1)^{p_i} \langle \psi_0(r^{(i)})\Psi \rangle_{r^{(i)}}. \quad (96)$$

Substituting Eq. (91) into Eq. (95), we can express Eq. (96) as

$$w(r_i) = u(r_i) - \int_0^\infty K(r_i|r_j)u(r_j)r_j^2 dr_j \quad (97)$$

where the kernel K is given by

$$K(r_i|r_j) = (-1)^{p_i+p_j+1} N \langle \psi_0(r^{(i)})\psi_0(r^{(j)}) \rangle_{r^{(ij)}}. \quad (98)$$

Here the integration is over $r^{(ij)}$, which denotes all coordinates except r_i and r_j ($i \neq j$). The kernel K can be expressed in terms of discrete and orthonormal set of eigenfunctions v_α

$$v_\alpha(r_1) = \lambda_\alpha \int_0^\infty K(r_1|r_2)v_\alpha(r_2)r_2^2 dr_2. \quad (99)$$

Some reflection will show that $K(r_1|r_2)$ can be written as

$$K(r_1|r_2) = \sum_{\beta=1}^{n_\lambda} \frac{v_\beta(r_1)v_\beta(r_2)}{\lambda_\beta}. \quad (100)$$

then substituting Eq. (100) in Eq. (99) the latter will be an identity. Using Eq. (100) in Eq. (97) allows $u(r_i)$ to be written

$$u(r_i) = \sum_{\lambda_\alpha=1} v_\alpha(r_i) \langle v_\alpha u \rangle + w(r_i) + \sum_{\lambda_\beta \neq 1} \frac{v_\beta(r_i) \langle v_\beta w \rangle}{\lambda_\beta - 1}. \quad (101)$$

Here v_β is the eigenfunction associated with λ_β and v_α with $\lambda_\alpha=1$. It can be verified that the first term in Eq. (101) does not contribute to the projection $\langle \Psi_0 P \Psi \rangle$ (cf. Refs. [29,30]). Thus we can write

$$\langle \Psi_0(r^{(1)}) P \Psi \rangle = \langle \psi_0^{(1)} \sum_{i=1}^{N+1} (-1)^{p_i} [w(r_i) + \sum_{\lambda_\beta} \frac{v_\beta(r_i) \langle v_\beta w \rangle}{\lambda_\beta - 1}] \psi_0(r^{(i)}) \rangle_{r^{(1)}}. \quad (102)$$

Substituting for $w(r_i)$ from Eq. (97) and rearranging, we get

$$\langle \Psi_0(r^{(1)}) P \Psi \rangle = \langle \psi_0^{(1)} | \sum_{i=1}^{N+1} [\psi_0(r^{(i)}) \langle \psi_0(r^{(i)}) + \sum_{\lambda_\alpha} \frac{v_\beta(r_i) \langle v_\beta w \rangle}{\lambda_\alpha - 1}] \Psi \rangle. \quad (103)$$

By comparing the left- and right-sides of Eq. (103), The expression for P can be extracted

$$P = \sum_{i=1}^{N+1} [\psi_0(r^{(i)}) \langle \psi_0(r^{(i)}) + \sum_{\lambda_\alpha} \frac{v_\alpha(r_i) \psi_0(r^{(i)}) \langle v_\alpha \psi_0(r^{(i)}) \rangle}{\lambda_\alpha - 1}]. \quad (104)$$

which implies

$$Q = 1 - \sum_{i=1}^{N+1} [\psi_0 \langle \psi_0 + \sum_{\lambda_\alpha} \frac{v_\alpha \psi_0 \langle v_\alpha \psi_0 \rangle}{\lambda_\alpha - 1}]. \quad (105)$$

These operators are symmetric in all $(N+1)$ -particle coordinates and they contain the dependence on space and spin of all coordinates explicitly. The main advantage of these expressions for P and Q , as compared to the heuristic form given by Feshbach, are they are complete and explicit. In addition they have been extended to scattering (including resonances) occurring in the inelastic domain (cf. Appendix B of Ref. [29]).

It has been shown in Ref. [30] that even though the above operators are not idempotent ($P^2 \neq P$ and $Q^2 \neq Q$) as operator identities that the matrix elements are equivalent $\langle \Phi_i P^2 \Phi_j \rangle = \langle \Phi_i P \Phi_j \rangle$ and $\langle \Phi_i Q^2 \Phi_j \rangle = \langle \Phi_i Q \Phi_j \rangle$ for any arbitrary antisymmetric functions Φ_i and Φ_j .

When the second term in Eq. (104) and the third term in Eq. (105) are dropped, we get the quasi-projection operators \hat{P} and \hat{Q} . These operators were employed by Temkin *et al.* [31] to calculate the resonance parameters of the $\text{He}^- [1s(2s)^2] {}^2S$ resonance (first observed by Schulz

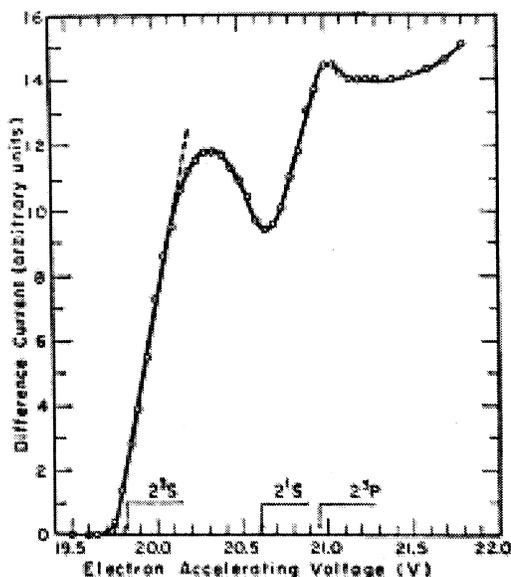


Figure 2: Metastable helium excitation from Schultz and Fox [35].

[32]), using open shell and closed shell target wave functions ϕ_0 and an angle-independent trial wave function as well as a configuration-interaction wave function containing up to 40 configurations. They obtained $E_{res}(^2S)=19.363$ eV plus a width $\Gamma=0.014$ eV. The difference between the results obtained by using the two different wave functions ϕ_0 is of the order of 0.02 eV. The resonance position agrees with the experimental result 19.31 ± 0.03 eV of Kuyatt *et al.* [33]. Calculations have also been carried out by Berk *et al.* [34] using target wave functions going up to a 10 term Hylleraas type wave functions and the full projection operators P and Q given in Eqs. (104) and (105). Again configuration interaction type wave functions containing up to 40 terms were employed obtaining resonance position of $(1s2s^2)^2S$ He $^-$ which is ~ 0.013 eV above the experimental position at 19.37 eV given by Schulz and Fox [35]. (That difference is presumably due to the uncalculated shift, which also occurs in the Feshbach theory.)

Now we come to 2P wide resonance in He $^-$ above the 3S threshold but below the 2S threshold of He, which has been first observed by Schulz and Fox [35](cf. Fig. 2).

Initially, it was thought to be a shape resonance because of its being above the 3S threshold. Bhatia and Temkin [36] used the same program which was used to calculate the 2S resonance below the 3S threshold and where quasi-projection operators were employed. Only those configurations in the trial wave functions were included which were orthogonal to the 3S state of He, thus avoiding the need to project out the 3S state. The calculations were carried out by using closed shell as well as open shell functions in the projection operators, giving the resonance position at 20.52489 and 20.56029 eV, respectively, for a trial wave function consisting of 40 terms. The position agrees with the result 20.536 eV obtained by Chung using his hole-projection technique [37]. The partial widths to 1S and 3S thresholds were found to be 0.0024 and 0.437 eV, and the calculation also showed that the total width is dominated by the decay to the (excited) $^2^3S$ state of He. These results also indicated that the resonance was a Feshbach resonance associated with the closed $^2^1S$ state of the target He rather than a shape resonance caused by the open $^2^3S$ state. An accurate calculation carried out by Junker [38] using the complex rotation method gave 20.33 and 0.575 eV for the position and width, respectively. These results agree with average experimental results

20.3±0.3 and total width 0.5 eV of Schultz and Fox [35], and Brunt *et al.* [39].

I shall not discuss here Dr. Temkin's (and collaborators') work on dispersion relations [40, 41] and in particular his work on threshold laws for electron-impact ionization of atoms and ions [which also apply to photon double (detachment/ionization) of (negative ions/atoms)]. The latter is discussed by Dr. R. Wehlitz in these Proceedings. A dispersion relation (DR) relates the real part of the scattering amplitude to an integral over the imaginary part, which in turn is proportional to total cross section. Such relations are important in judging the consistencies and accuracy of both theoretical calculations and experimental measurements. The problem in electron-atom scattering has been to correctly include the effects of exchange. Dr. Temkin has proposed using partial wave dispersion relations to solve this problem. At this point the correct partial wave DR have been constructed both approximately [42] and exactly [43] in the static-exchange approximation.

Up to now, I have described some of Dr. Temkin's important contributions in electron-atom scattering and associated problems in atomic physics mentioned above. He has also made important contributions in the field of electron-molecule scattering: Briefly stated, Dr. Temkin (with various coworkers) introduced the "fixed nuclei" approximation (as well as the name) in electron-(diatomic) molecule scattering [44,45]. They showed that the (partial wave) scattering amplitude could be expressed as the product of the two factors; one of which depends on scattering parameters resulting from the dynamical interaction of the electron with the molecule, which is most conveniently calculated in the body-frame of the molecule, and a second factor, depending on geometrical functions representing the rotation of the scattering angles from the body to the lab frame. The cross sections, averaged over orientations of the internuclear axis could then be expressed as a sum of scattering parameters multiplied by spherical harmonics together with vector coupling coefficients. A second contribution concerns the "adiabatic nuclei" approximation, originally introduced by Chase [46] in the context of nuclear physics. Chase showed that in a cogent approximation that the amplitude for rotational excitation can be expressed as a matrix element of the fixed-nuclei amplitude between initial and final rotational states. Because the dependence on the orientation is analytic (actually \mathcal{D} function), these integrals can also be done analytically, again - first - by Temkin and coworkers [46,47]. (The name adiabatic-nuclei was also coined by Temkin [48].) Temkin was also involved in other developments, most notably the hybrid theory [49], which will further be discussed by Dr. B. I. Schneider in his contribution to these Proceedings.

Having described some of Dr. Temkin's work, I now will describe some of the work carried out by Dr. Drachman. Perhaps, after Sir Harrie Massey, Dr. Drachman has not only made important contributions to positron physics but has also made it a popular subject of research.

Scattering of Positrons from Hydrogen Atoms

Calculation of positron-hydrogen scattering at low energies can be carried out by the method of polarized orbitals as in the case of e-H scattering. Instead, Drachman [50], employing a variation of the method, chose the wave function of the form

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = u(\mathbf{r}_1)[1 + G(\mathbf{r}_1, \mathbf{r}_2)]\phi_0(\mathbf{r}_2). \quad (106)$$

The function $G(\mathbf{r}_1, \mathbf{r}_2)$, correct to first order in the potential

$$V(\mathbf{r}_1, \mathbf{r}_2) = \frac{2}{r_1} - \frac{2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (107)$$

has been determined by Dalgarno and Lynn [51] as a solution of the differential equation

$$[G, H(2)]\phi_0(\mathbf{r}_2) = (V - \langle V \rangle)\phi_0(\mathbf{r}_2) \quad (108)$$

where

$$H(2)\phi_0(\mathbf{r}_2) = [-\nabla_2^2 - \frac{2}{r_2}]\phi_0(\mathbf{r}_2) = -\phi_0(\mathbf{r}_2), \quad (109)$$

and

$$\langle V \rangle = \int d\mathbf{r}_2 \phi_0(\mathbf{r}_2) V(\mathbf{r}_1, \mathbf{r}_2) \phi_0(\mathbf{r}_2). \quad (110)$$

The function G includes all multipoles ≥ 0 . The adiabatic equation, correct to second order in V , is given by

$$[-\nabla_1^2 - k^2 + v_{st} + V_2]u(\mathbf{r}_1) = 0. \quad (111)$$

In the derivation of the above equation, we have taken $\langle G \rangle = 0$. Here

$$v_{st} = 2e^{-2r_1} \left(1 + \frac{1}{r_1}\right), \quad (112)$$

and

$$\begin{aligned} V_2 &= r_1^{-2} [5 - (4r_1^2 + 8r_1 + 10)e^{-2r_1} + (4r_1^3 + 7r_1^2 + 8r_1 + 5)e^{-4r_1} \\ &\quad - 2(r_1 + 1)^2 (e^{-2r_1} + e^{-4r_1}) (\text{Ei}[2r_1] - 2\ln[2\gamma r_1]) \\ &\quad - 2\text{Ei}[-2r_1] ([r_1 - 1]^2 e^{2r_1} + [r_1^2 + 2r_1 - 3] + 4[r_1 + 1]e^{-2r_1})], \end{aligned} \quad (113)$$

where $\ln\gamma=0.57721$ is the Euler's constant and

$$\text{Ei}[-z] = - \int_z^\infty \frac{e^{-y}}{y} dy. \quad (114)$$

For small value of r_1 , $v_{st} \rightarrow 2r_1^{-1} - 2$ and $V_2 \rightarrow -1$, while for $r_1 \rightarrow \infty$ $V_2 = -4.5r^{-4}$. Eq. (111) can be solved for various values of k to determine the phase shifts and the results are given in Fig. 3. For $k=0$, the scattering length requires a correction due to the long-range potential [11], as indicated in Eq. (34), and its value is -2.54 versus Schwartz's -2.10 [7], which is the upper bound on the scattering length. This shows that the potential in Eq. (113) is too attractive. Drachman [50] modified the potential to

$$v_{st} + V_2 + (\alpha - 1)V_{20}, \quad (115)$$

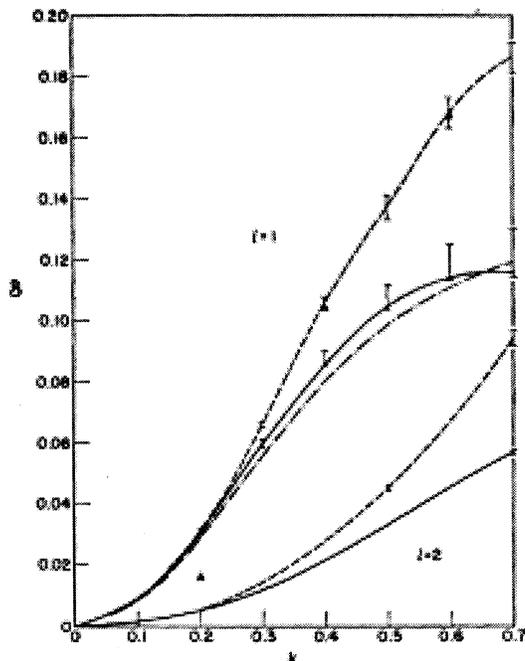


Figure 3: Phase shifts in radians for p - and d -wave scattering. The solid curves are for $\alpha=0.1$, and the vertical bars indicate $\alpha=1.0$ and $\alpha=0$ limits. The triangles are Brandsden's p -wave values (Ref. [52]).

where V_{20} is the monopole part of V_2 . The complete suppression of monopole or short-range part of the potential, i.e., $\alpha=0$ gives scattering length -2.07 , in good agreement with Schwartz's value. Drachman calculated P -wave and D -wave phase shift for various values of k and found reasonable agreement with those of Brandsen [52] (cf. Fig. 3).

In the same calculation, Drachman concluded, from the change of sign of the scattering length with increasing mass of the positron, that there is no bound state of the system e^+e^-P unless the mass of the positron is $3.6m_e$ for $\alpha=0.1$, while for $\alpha=1$ it is about $3.1m_e$.

Houston and Drachman [53] using a more flexible wave function than that of Schwartz [7] in the Kohn variational method, obtained an upper-bound scattering length $a \leq -2.10278$. They obtained an extrapolated estimate $a = -2.1036 \pm 0.0004$. These results are in good agreement with Schwartz's result $a \leq -2.10$. They applied the Harris method [54] to obtain S -wave phase shifts at nonzero energies which are in good agreement with those obtained by the Feshbach formalism [16] described below.

One of my first calculations with Drachman [55] was the S -wave elastic scattering of positrons (e^+) from hydrogen atoms below the positronium pickup threshold. As mentioned above for electron-hydrogen scattering, rigorous lower bounds have been obtained using the Feshbach projection formalism [16]. Similarly, the results for e^+H have rigorous lower bounds. Since there is no exchange between a positron (labeled 1) and an electron (labeled 2) in the hydrogen atom in this process, the projection operators P and Q are defined as

$$P = |\phi_0(r_2) \rangle \langle \phi_0(r_2)|, \quad (116)$$

$$Q = 1 - P, \quad (117)$$

such that P operating on the wave function does not change its asymptotic form in the limit $r_1 \rightarrow \infty$

$$P\Psi = \Psi. \quad (118)$$

TABLE V. e^+ -H phase shifts for S -wave scattering for various k .

k	S -wave				P -wave	
	Schwartz [7]	η_{extrap}	$\Delta\eta$	η_{final}	Armstead ^a [8]	η_{final}
0.1	0.151	0.148085	0.000223	0.1483	0.008,0.009(1)	0.0094
0.2	0.188	0.187496	0.000200	0.1877	0.032,0.033(1)	0.0338
0.3	0.168	0.167407	0.000306	0.1677	0.064,0.065(1)	0.0665
0.4	0.120	0.119724	0.000420	0.1201	0.099,0.102(1)	0.1016
0.5	0.062	0.061934	0.000429	0.0624	0.130,0.132(1)	0.1309
0.6	0.007	0.003191	0.000689	0.0039	0.153,0.156(2)	0.1547
0.7	-0.054	-0.052183	0.000980	-0.0512	0.175,0.178(3)	0.1799

^a Armstead [8] has given two sets of results. The first entry gives his converged results while the second entry his estimate of most probable results with uncertainty in the last figure given in parenthesis.

Here Ψ is given by

$$\Psi_L(\mathbf{r}_1, \mathbf{r}_2) = u_L(\mathbf{r}_1)\phi_0(\mathbf{r}_2) + \Phi(\mathbf{r}_1, \mathbf{r}_2), \quad (119)$$

where the generalized Hylleraas function is

$$\Phi = e^{-(\delta r_1 + \gamma r_2 + \alpha r_{12})} \sum_{lmn}^N C_{lmn} r_1^l r_2^m r_{12}^n. \quad (120)$$

In the absence of exchange, the e^+ -H problem should be easy to solve but not so due to the virtual positronium formation. Therefore, we have included $e^{-\alpha r_{12}}$ in Φ , where r_{12} is the distance between the positron and the electron. An integro-differential equation of the form Eq. (81) ($V_{ex}=0$ here) is solved for the scattering functions $u_L(r_1)$ and phase shifts η_L are obtained in the limit $r_1 \rightarrow \infty$ from

$$u_L(r_1) = \sin(kr_1 - L\pi/2 + \eta_L). \quad (121)$$

It should be pointed out that the phase shifts are negative in the absence of the optical potential. The inclusion of the optical potential, which is attractive as in the e-H scattering, increases the phase shifts from the values obtained in the presence of only the repulsive static potential v_{st} in Eq. (81). The phase shifts were calculated for up to $N=84$ and extrapolated for $N \rightarrow \infty$. These phase shifts plus a correction $\Delta\eta$ for the long-range polarization potential are compared in Table V with those obtained by Schwartz [7] using the Kohn variational principle. The long-range effects

are not well included in a Hylleraas type correlation functions and therefore have to be calculated separately. Our final results ($\eta_{\text{final}} = \eta_{\text{extrapolated}} + \Delta\eta$), which, we believe, are accurate within ± 0.0002 radians, differ at $k=0.6$ and 0.7 from those obtained by Schwartz [7].

A similar calculation [56] has been carried out for P -wave scattering. Here the closed channel function is given by

$$\Phi = f_1 \cos\left(\frac{1}{2}\theta_{12}\right) \mathcal{D}_1^{1+} + f_2 \sin\left(\frac{1}{2}\theta_{12}\right) \mathcal{D}_1^{1-}. \quad (122)$$

The f_i are taken of the Hylleraas type with two non-linear parameters:

$$f_1 = e^{-(\delta_1 r_1 + \gamma_1 r_2)} \sum_{l \geq 1} \sum_{m \geq 0} \sum_{n \geq 0} C_{lmn}^{(1)} r_1^l r_2^m r_{12}^n, \quad (123)$$

and

$$f_2 = e^{-(\delta_2 r_1 + \gamma_2 r_2)} \sum_{l \geq 1} \sum_{m \geq 0} \sum_{n \geq 0} C_{lmn}^{(2)} r_2^l r_1^m r_{12}^n. \quad (124)$$

The f_i are linearly independent functions because the positron and the electron are distinguishable. Now there are four nonlinear parameters to be varied to get the best results. The maximum number of terms for each f is 84, giving a total of 168 terms in Φ . Here we have added the dipole adiabatic and the quadrupole plus nonadiabatic corrections to the extrapolated phase shifts. Our final results are compared to those of Armstead [8] in Table V. The rigorous lower bound is lost due to the addition of corrections for the long-range potential. Nevertheless, the results still are accurate.

Needless to say, these results have stood the test of the time and are still considered to be the benchmark results.

Annihilation of Positrons with Electrons, Z_{eff}

An important process is the annihilation in flight of positrons by atomic hydrogen resulting in the 511 KeV line which has been observed in solar flares [57] and from the galactic center [58]. This line can be used to infer properties of flares and the solar plasmas. Having calculated the wave functions for the scattering of positrons from hydrogen atoms, the partial cross sections for annihilation can be calculated from the expression given below [59]

$$\sigma_a = Z_{\text{eff}} \frac{\alpha^3}{k} (\pi a_0^2), \quad (125)$$

where α is the fine-structure constant, a_0 is the Bohr radius, and k is the incident positron momentum in units of a_0^{-1} . The quantity Z_{eff} , which is the measure of the probability that the positron and electron are at the same point, depends on specific properties of the positron-atom system. Z_{eff} is equal to Z , the number of electrons in the atom, when the positron can be represented as a free particle. For the hydrogen atom

$$Z_{\text{eff}} = \int \int d\mathbf{r}_1 d\mathbf{r}_2 |\Psi(\mathbf{r}_1, \mathbf{r}_2)|^2 \delta(\mathbf{r}_1 - \mathbf{r}_2), \quad (126)$$

where $\Psi(\mathbf{r}_1, \mathbf{r}_2)$ is the positron-hydrogen wave function. It should be noted that for the calculation of Z_{eff} , $u_L(\mathbf{r})$ should have a plane wave normalization, i.e.,

$$u_L(\mathbf{r}) = (2L + 1) \frac{\sin(kr - \frac{1}{2}L\pi + \eta_L)}{kr} P_L(\cos(\theta)) \quad (127)$$

We present Z_{eff} for $L=0$ and 1 [60,61] in Table VI and compare them with those obtained by Humberston and Wallace [62] and Humberston [63]. For $L > 1$, we use the plane wave expansion for the incident positron

$$Z_{eff}(L > 1) \cong \sum_{L=2}^{\infty} (2L + 1) \int_0^{\infty} dr r^2 \phi_0^2(r) j_L^2(kr). \quad (128)$$

Using the identity

$$\sum_{L=0}^{\infty} (2L + 1) j_L^2 = 1 \quad (129)$$

we get [with $\phi_0(r) = 2e^{-r}$]

$$\begin{aligned} Z_{eff}(L > 1) &= 4 \int_0^{\infty} dr r^2 e^{-2r} (1 - j_0^2 - 3j_1^2) \\ &= \frac{k^2}{k^2 + 1} + \frac{6}{k^2} \left(\frac{1}{k^2} \ln(1 + k^2) - \frac{1 + k^2/2}{1 + k^2} \right). \end{aligned} \quad (130)$$

We give the total Z_{eff} in Table VI.

Table VI. Z_{eff} for e^+ -H annihilation. $k=0$ results are from Ref. [64,65].

k	L=0		L=1		$Z_{eff}(\text{Total})$
	$Z_{eff}(L=0)$	Ref. [62]	$Z_{eff}(L=1)$	Ref. [63]	
0					8.868
0.1	7.363	7.5	0.13008	0.1335	7.493
0.2	5.538	5.7	0.53994	0.5366	6.079
0.3	4.184	4.3	1.12441	1.114	5.312
0.4	3.327	3.3	1.76292	1.719	5.100
0.5	2.730	2.7	2.33910	2.353	5.091
0.6	2.279	2.3	2.84988	2.823	5.168
0.7	1.950		3.67030	3.637	5.683

We can calculate the thermally averaged annihilation parameter

$$\bar{Z}(T) = \int_0^{\infty} dk f_T(k) Z_{eff}(k), \quad (131)$$

where $f_T(k)$ is the Maxwell-Boltzman distribution function. We can fit the calculated $Z_{eff}(k)$ to a sixth-degree polynomial of the form

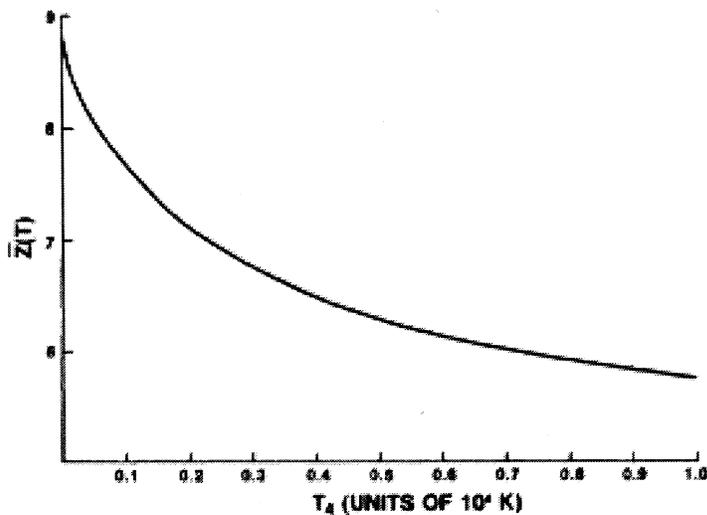


Figure 4: Thermally averaged annihilation parameter $\bar{Z}(T)$ obtained from the polynomial fit $Z_{eff}(k)$.

$$Z_{eff}(k) = \sum_0^6 Z_n k^n. \quad (132)$$

Using this expansion, the integration in Eq. (131) can be carried out analytically and we have

$$\bar{Z}(T) = \sum_{n=0}^6 \bar{Z}_n (T_4)^{n/2}, \quad (133)$$

where T_4 is the temperature in units of 10^4 K and

$$\bar{Z}_n = \alpha_n Z_n A_0^{-n/2}. \quad (134)$$

Here $A_0=15.789$ and Z_n , \bar{Z}_n , and α_n are given in Table VII.

Table VII. Coefficients of the polynomial, Z_n , \bar{Z}_n , and α_n .

n	Z_n	\bar{Z}_n	α_n
0	8.868	8.868	1
1	-7.38	-2.226	$2\pi^{-1/2}$
2	-102.77	-9.763	$\frac{3}{2}$
3	527.38	18.971	$4\pi^{-1/2}$
4	-978.68	-14.722	$\frac{16}{4}$
5	773.15	5.284	$12\pi^{-1/2}$
6	-197.17	-0.658	$\frac{105}{4}$

Now $\bar{Z}(T)$ can be calculated at any temperature (cf. Fig. 4).

e^+ -He Scattering

Although accurate calculations for e^+ -H can be carried out because wave functions of hydrogen atoms are known exactly it is difficult to perform experiments on this system. On the other hand, e^+ -He experiments can be performed relatively easily but the calculations are rather tedious because elaborate He functions are difficult to employ. However, Houston and Drachman [53] used those simple wave functions which gave a reasonable value of the polarizability of the He atom. They used the Harris method [54] to calculate phase shifts at low energies and their results agreed with the results of the variational calculation of Drachman [65]. They added a term to the wave function to represent the long-range dipole potential and obtained scattering length $a=-0.524$ and $Z_{eff}=4.3$ at $k^2=0$, using the Kohn variational method.

Properties of Ps^- and Photodetachment

The positronium negative ion (Ps^-), consisting of two electrons and a positron, is particle stable and decays only by e^+e^- annihilation into gamma rays. Mills [66,67] has produced and detected this ion and measured its lifetime. Drachman and I [68] calculated its ground state (1S) energy by using a trial function of the Hylleraas form, calculated expectation values of delta functions, and cusp conditions given by

$$\nu_i = \left\langle \delta(\mathbf{r}_i) \frac{\partial}{\partial r_i} \right\rangle < \delta(\mathbf{r}_i) >^{-1}, \quad (135)$$

$$\nu_{12} = \left\langle \delta(\mathbf{r}_{12}) \frac{\partial}{\partial r_{12}} \right\rangle < \delta(\mathbf{r}_{12}) >^{-1}. \quad (136)$$

Table VIII. Binding energy (Ry) of 1S state of Ps^- , expectation values of δ functions, cusp conditions, and decay rate Γ ((nsec) $^{-1}$). [The notation $A(-B)$ stands for $A \times 10^{-B}$.]

N	γ	δ	Binding energy	$\delta(\mathbf{r}_i)$	$\delta(\mathbf{r}_{12})$	ν_i	ν_{12}	Γ
125	0.2585	0.3585	0.024009788	0.020722	1.7151(-4)	-0.49910	0.49711	2.0850
161	0.3700	0.3700	0.024010026	0.020732	1.7136(-4)	-0.49986	0.49695	2.0860
202	0.380	0.380	0.024010089	0.0200730	1.7129(-4)	-0.49740	0.49740	2.0858
120	0.604	0.296	0.024009966	0.020733	1.7190(-4)	-0.50000	0.49347	2.0861
165	0.604	0.314	0.024010079	0.020773	1.7164(-4)	-0.49999	0.49441	2.0861
220	0.604	0.313	0.024010113	0.020733	1.7150(-4)	-0.50000	0.49508	2.0861

Here r_1 and r_2 are the relative distances of electrons 1 and 2 with respect to the positron, and $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$. Results are in given in Table VIII for the Hylleraas wave functions (see Eq. (141) below) with up to $N=203$ with $\gamma = \delta$, and up to 220 terms with $\gamma \neq \delta$, respectively. These functions have been used to calculate other properties. The cusp conditions test the accuracy of the wave functions near points of coalescence, since $\nu_1 = \nu_2 = -\frac{1}{2}$ and $\nu_{12} = +\frac{1}{2}$ for exact solutions of the Schrödinger equation. The convergence of results, given in Table VIII, shows that our wave functions should be fairly accurate. To a sufficient accuracy the Ps^- decay rate is given by

$$\begin{aligned}\Gamma &= 2\pi\alpha^4(c/a_0)[1 - \alpha(17/\pi - 19\pi/12)] \langle \delta(\mathbf{r}_1) \rangle \\ &= 100.6174 \langle \delta(\mathbf{r}_1) \rangle \text{ (nsec)}^{-1},\end{aligned}\quad (137)$$

where the correction term proportional to α is due to the triplet lifetime [69] and the leading radiative correction to the singlet lifetime [70]. Our calculated value is in agreement with the measured [67] value $\Gamma = 2.09 \pm 0.09(\text{nsec})^{-1}$.

Mills [71] recognized that the existence of $^3P^e$ state of positronium, as in H^- [72], would have interesting experimental consequences: The state would be metastable against breakup because $Ps^-(^3P^e) \rightarrow Ps(^1S) + e^-$ is nonrelativistically forbidden. Using 70-term Hylleraas wave function, Mills [71] did not find such a state. We [68] too failed to find this state even when we used larger expansions and also included long-range terms of several types [73].

Photodetachment of Ps^-

Mills [66] suggested that Ps^- ion could be used to generate positronium (Ps) beams of controlled energy; this would involve acceleration of Ps^- ions and photodetachment of one electron. Drachman and I [74] calculated the dipole transition matrix elements by two simplifications: the initial Ps^- wave function is represented by an asymptotic form whose normalization comes from our most accurate wave function [68], and the final state is a plane wave.

The Hamiltonian of the system consisting of two electrons (ρ_1, ρ_2) and one positron (\mathbf{x}) is

$$H = -\nabla_{\rho_1}^2 - \nabla_{\rho_2}^2 + \nabla_{\mathbf{x}}^2 - \frac{1}{|\rho_1 - \mathbf{x}|} - \frac{1}{|\rho_2 - \mathbf{x}|} + \frac{1}{|\rho_1 - \rho_2|}.\quad (138)$$

The center-of-mass system is

$$\mathbf{R} = \frac{1}{3}(\rho_1 + \rho_2 + \mathbf{x}), \quad \mathbf{r}_1 = \rho_1 - \mathbf{x}, \quad \mathbf{r}_2 = \rho_2 - \mathbf{x},\quad (139)$$

where \mathbf{R} is the coordinate of the center of mass of the entire system, \mathbf{r}_1 and \mathbf{r}_2 are the distances of electrons 1 and 2 from the positron, respectively. The Hamiltonian is given by

$$H = -\frac{1}{3}\nabla_{\mathbf{R}}^2 - 2 \left[\nabla_{\mathbf{r}_1}^2 + \nabla_{\mathbf{r}_2}^2 + \nabla_{\mathbf{r}_1} \cdot \nabla_{\mathbf{r}_2} + \frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} \right].\quad (140)$$

Omitting the center of mass coordinate \mathbf{R} , which describes uniform motion of the center of mass, we write a wave function for the Ps^- ground state in the Hylleraas form

$$\Psi_i(\mathbf{r}_1, \mathbf{r}_2) = \Psi_i(r_1, r_2, r_{12}) = \frac{1}{\sqrt{8\pi^2}} \sum_{lmn} [r_1^l r_2^m e^{-\gamma r_1 - \delta r_2} + r_2^l r_1^m e^{-\gamma r_2 - \delta r_1}] r_{12}^n.\quad (141)$$

The final state consists of an electron in a p state moving away relative to the center-of-mass of the Ps atom. We use the coordinate $\mathbf{R}_2 = \mathbf{r}_2 - \mathbf{r}_1/2$ in place of \mathbf{r}_2 , while retaining \mathbf{r}_1 as the distance between the positron and electron. The Hamiltonian for these asymmetric coordinates is

$$H = -2 \left[\nabla_{\mathbf{r}_1}^2 + \frac{3}{4} \nabla_{\mathbf{R}_2}^2 + \frac{1}{r_1} + \frac{1}{|\mathbf{R}_2 + \frac{1}{2}\mathbf{r}_1|} - \frac{1}{|\mathbf{R}_2 - \frac{1}{2}\mathbf{r}_1|} \right]. \quad (142)$$

The final state is given by the p -wave part of the symmetrized product of a plane wave in relative coordinates:

$$\Psi_f = \frac{1}{\sqrt{2}} [\phi(\mathbf{r}_1) e^{i\mathbf{k}\cdot\mathbf{R}_2} + \phi(\mathbf{r}_2) e^{i\mathbf{k}\cdot\mathbf{R}_1}], \quad (143)$$

where $E = \frac{3}{2}k^2$. The photodetachment cross section in the velocity form can be written as [75]

$$\sigma_v = \frac{2k\alpha a_0^2}{9\omega} |\langle \Psi_f | Q_V | \Psi_i \rangle|^2, \quad (144)$$

where the dipole transition operator in the velocity form is

$$Q_V = 2\hat{\mathbf{k}} \cdot (\nabla_{\rho_1} + \nabla_{\rho_2} - \nabla_{\mathbf{x}}), \quad (145)$$

and ω is energy of the incident wave. The finite mass of the positron gives a factor of $\frac{2}{3}$ when compared with the photodetachment expression for an infinitely massive atomic ion. The cross section in the length form can be written as [75]

$$\sigma_L = \frac{2k\omega\alpha a_0^2}{9} |\langle \Psi_f | Q_L | \Psi_i \rangle|^2, \quad (146)$$

where the dipole operator in the length form is

$$Q_L = \hat{\mathbf{k}} \cdot (\rho_1 + \rho_2 - \mathbf{x}). \quad (147)$$

These transition operators can be written in terms of the unsymmetric coordinates:

$$Q_V = \hat{\mathbf{k}} \cdot \left(\frac{2}{3} \nabla_{\mathbf{R}} + 4\nabla_{\mathbf{r}_1} + 2\nabla_{\mathbf{R}_2} \right). \quad (148)$$

and

$$Q_L = \hat{\mathbf{k}} \cdot \left(\mathbf{R} + \mathbf{r}_1 + \frac{2}{3} \mathbf{R}_2 \right). \quad (149)$$

Now we represent the initial loosely bound state function in the following form [76,77]:

$$\Psi_i = C \frac{e^{-\gamma R_j}}{R_j} \phi(r_k), \quad \text{for } R_j \gg r_k, \quad (150)$$

where $\gamma=0.12651775$ from our best variational value [68] of the Ps^- binding energy 0.024010113 Ry.

$$C(r) \equiv \sqrt{8\pi r} e^{\gamma r} \Psi_i(0, r, r). \quad (151)$$

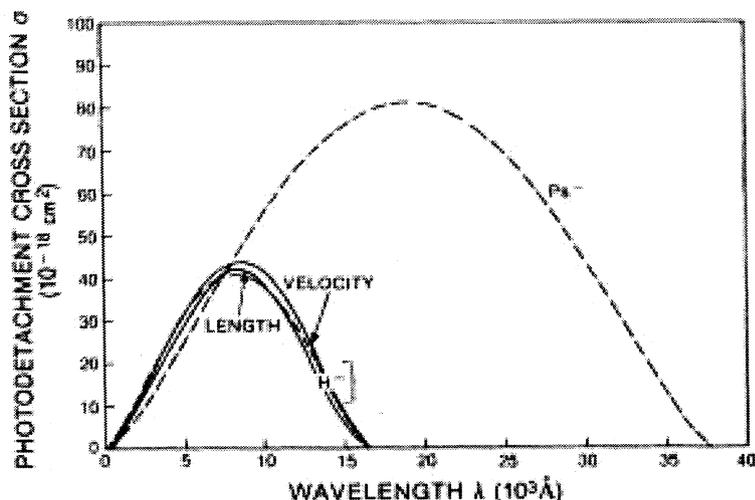


Figure 5: Photodetachment cross sections (dashed lines) in the asymptotic approximation for Ps^- and H^- as functions of wavelengths of the incident light. The length and velocity forms of the H^- cross sections are from more elaborate theory of K. L. Bell and A. E. Kingston [78] (solid lines).

We find $C=0.1856(2)$ (cf. Ref. [74] for details). We find

$$\sigma_V = \sigma_L = (3.8245 \times 10^{-17} \text{cm}^2) \frac{k^3 C^2}{(k^2 + \gamma^2)^3}, \quad (152)$$

which can be written as

$$\sigma = (1.32 \times 10^{-18} \text{cm}^2) \frac{k^3}{(k^2 + \gamma^2)^3}. \quad (153)$$

We can write the cross section in terms of the wave length of the incident light,

$$\sigma = (650 \times 10^{-18} \text{cm}^2) \left(\frac{\lambda}{\lambda_0}\right)^{3/2} \left(1 - \frac{\lambda}{\lambda_0}\right)^{3/2}, \quad \text{for } \lambda \leq \lambda_0, \quad (154)$$

where $\lambda_0=37953.46 \text{ \AA}$. In Fig. 5 we have plotted the present results [Eq. (154)], compared with the corresponding results [77] for H^- . In the latter case the asymptotic approximation is seen to compare fairly well with the more elaborate calculations of Bell and Kingston [78], and we expect the present results to be similarly reliable.

A scattering calculation for the final state has been carried out by Ward, Humberston and McDowell [79] to calculate the photodetachment cross section of Ps^- . See the article by Dr. S. J. Ward in these Proceedings.

Muonic Molecules

There have been speculations of the possibility of realizing useful muonic catalyzed fusion. The Born-Oppenheimer approximation has been used traditionally to calculate energy levels of muonic

systems. Drachman and I [80], for the first time, using Hylleraas type wave functions for such systems, carried out straightforward Rayleigh-Ritz variational calculations and showed that the binding energy of even the weakly bound $td\mu$ molecular state of the angular momentum equal to 1 and vibrational state 1 ($J = 1, v = 1$) can be obtained fairly accurately. We [81] further studied the deexcitation of $td\mu$ muonic molecule by internal conversion and also calculated the $J = 2$ binding energy. We wrote an easy-to-read review article [82] on this subject. I will not discuss further our work because Prof. E. A. G. Armour has carried out extensive work on muonic systems and has written an article on muonic physics which appears in these Proceedings.

Polarizabilities of Two-Electron Systems

We will see in the subsequent section that in order to calculate the Rydberg levels of three-electron systems, the interaction between valence electron and core should be known. This interaction can be represented by the potential

$$U(x) = -\frac{\alpha_1}{x^4} + \frac{6\beta_1 - \alpha_2}{x^6} + \text{higher - order terms}, \quad (155)$$

where x is the relative distance between the valence electron and the core, and α_1 and α_2 are dipole and quadrupole polarizabilities, respectively, and β_1 is the first nonadiabatic coefficient. These polarizabilities, in the second-order perturbation calculations, are given by the general expression

$$S_{k,i} = \sum_N \frac{\langle 0|v_i|N \rangle \langle N|v_i|0 \rangle}{(E_N - E_0)^k}, \quad (156)$$

where $|0 \rangle$ represents the ground state of the core and $|N \rangle$ intermediate states, determined by diagonalizing the appropriate Hamiltonian. We can write

$$S_{1,i} \equiv \alpha_i = \sum_N \frac{\langle 0|v_i|N \rangle \langle N|v_i|0 \rangle}{(E_N - E_0)}, \quad (157)$$

$$S_{2,i} \equiv \beta_i = \sum_N \frac{\langle 0|v_i|N \rangle \langle N|v_i|0 \rangle}{(E_N - E_0)^2}, \quad (158)$$

and

$$S_{3,i} \equiv \gamma_i = \sum_N \frac{\langle 0|v_i|N \rangle \langle N|v_i|0 \rangle}{(E_N - E_0)^3}. \quad (159)$$

The potential between the valence electron at a distance x from the nucleus and the core can be expanded in the form

$$V \simeq \frac{v_1}{x^2} + \frac{v_2}{x^3} + \dots \quad (160)$$

where

$$v_1 = 2 \left[1 + \frac{K(Z-2)}{2} \right] (\mathbf{w} \cdot \hat{\mathbf{x}}), \quad (161)$$

and

$$v_2 = 2 \left[r_1^2 P_2(\hat{\mathbf{r}}_1 \cdot \hat{\mathbf{x}}) + r_2^2 P_2(\hat{\mathbf{r}}_2 \cdot \hat{\mathbf{x}}) - K w^2 P_2(\hat{\mathbf{w}} \cdot \hat{\mathbf{x}}) \right]. \quad (162)$$

Here $\mathbf{w} = \mathbf{r}_1 + \mathbf{r}_2$, $K = 2/(1+M)$, M is the nuclear mass, and Z is the nuclear charge. Drachman and I [83] calculated various quantities in Eq. (156) using the pseudostate summation method. We used Hylleraas type wave functions for the ground state and intermediate states. The nonlinear parameters in intermediate states are optimized by maximizing α_1 , which according to the variational principle, has a lower bound to the exact α_1 . In Table IX, we give our results for various ions.

Table IX. Adiabatic and nonadiabatic polarizabilities for three isoelectronic systems. $\Lambda(-B)$ implies $\Lambda \times 10^{-B}$

System	Li ⁺	Be ²⁺	B ³⁺
α_1	0.192485	0.052282	0.019651
β_1	0.03529	4.919(-3)	1.125(-3)
γ_1	6.806(-3)	4.847(-4)	6.723(-5)
α_2	0.11389	0.01532	3.427(-3)
β_2	0.01668	1.132(-3)	1.524(-4)
γ_2	2.584(-3)	8.819(-5)	7.136(-6)

Polarizabilities of He and H⁻

We now turn to calculations of such quantities for He and H⁻, where the convergence is rather slow for He and even slower for H⁻. For He, we [84] used up to 525 terms for the ground state, 364 terms for the *P*-wave intermediate states. For *D*-wave intermediate states, both *sd* and *pp* terms are required, and therefore we used up to 165 *sd* terms and up to 56 *pp* terms in our wave function. In Table X, we show our final results for He.

Table X. Adiabatic and nonadiabatic polarizabilities for ⁴He. We also give the estimated errors.

k	$i=1$ (Dipole)	$i=2$ (Quadrupole)
1	$\alpha_1=1.383\ 241\ 013\ 80 \pm 10$	$\alpha_2=2.443\ 372\ 616\ 06 \pm 20$
2	$\beta_1=0.707\ 521\ 492\ 749 \pm 55$	$\beta_2=1.035\ 440\ 519\ 03 \pm 20$
3	$\gamma_1=0.375\ 538\ 368\ 413 \pm 21$	$\gamma_2=0.467\ 345\ 191\ 67 \pm 23$

Since we include the mass polarization term in the Hamiltonian, it is interesting to see how large an effect this has on various polarizabilities. Therefore, we carried out our calculations, using the largest expansion lengths, for $K=0$ and for finite K , both for ⁴He and ³He. We present the results in Table XI.

Table XI. Effect of the finite nuclear mass on the polarizabilities of both isotopes of helium. Δ is the difference between the results for finite and infinite mass.

Quantity	$\Delta(^3\text{He})$	$\Delta(^4\text{He})$
α_1	6.4798(-5)	4.88345(-5)
β_1	1.5044(-5)	1.1341(-5)
γ_1	4.5918(-6)	3.4638(-6)
α_2	-2.270054(-3)	-1.7107096(-3)
β_2	-8,70263(-4)	-6.55793(-6)
γ_2	-3.64039(-4)	-2.74316(-4)

We carried out a similar calculation for H^- for finite K , except that in this case we used 615 terms in the ground state wave function. The quantities are much larger than in the case of He and the results are given in Table XII.

Table XII. Adiabatic and nonadiabatic polarizabilities for H^- . We also give the estimated errors.

k	$i=1(\text{Dipole})$	$i=2(\text{Quadrupole})$
1	$\alpha_1=206.148\ 7618\pm 37$	$\alpha_2=7766.79\ 374\pm 48$
2	$\beta_1=1886.699\ 325\pm 34$	$\beta_2=70\ 155.536\ 09\pm 25$
3	$\gamma_1=20\ 046.0671\pm 30$	$\gamma_2=711\ 88.8802\pm 96$

To check the accuracy of our results, we consider two special cases, related to $S_{0,1}$ and $S_{1,-1}$. The first one tests the completeness of pseudostates that we are using without considering the ground-state accuracy:

$$\sum_N \langle 0|\mathbf{w} \cdot \hat{\mathbf{x}}|N \rangle \langle N|\mathbf{w} \cdot \hat{\mathbf{x}}|0 \rangle = \langle 0|(\mathbf{w} \cdot \hat{\mathbf{x}})^2|0 \rangle \quad (163)$$

Comparison between the left and right sides of Eq. (163) gives a measure of completeness of the set N . We give results in Table XIII, along with the difference of the ratio from unity.

Table XIII. Comparison between left and right side of Eq. (163). Δ =difference of the ratio from unity.

System	left hand side	right hand side	Δ
He	0.752 552 891 661	0.752 552 891 770	1.0(-9)
H^-	7.488 423 814 28	7.488 424 910 34	1.5(-7)

The second test is the Thomas-Reiche-Kuhn sum rule, which for the finite-nuclear mass takes the form

$$\sum_N \langle 0|\mathbf{w} \cdot \hat{\mathbf{x}}|N \rangle \langle N|\mathbf{w} \cdot \hat{\mathbf{x}}|0 \rangle (E_N - E_0) = 2 + K \quad (164)$$

Now the extent of the agreement between the left and right sides of Eq. (164) measures both the accuracy of the ground state $|0 \rangle$ and the completeness of intermediate states $|N \rangle$. We find

the ratio of the left side to the right side is 0.999 999 87 for He, and the corresponding ratio for H^- is 0.999 9787, respectively. All these tests show that H^- is a more sensitive system than He. Nevertheless, our results are accurate to the accuracy given.

Polarizabilities of H_2^+ and D_2^+

Having calculated polarizabilities of two-electron systems, it must appear that there should be no difficulty in calculating polarizabilities of molecular ions H_2^+ and D_2^+ , the only difference being that two light particles have been replaced by two heavy particles and the mass-polarization term becomes as important as other kinetic energy terms in the Hamiltonian. Since, with a hammer in hand the whole world looks like a nail, I just went ahead with the calculations for H_2^+ and D_2^+ systems using Hylleraas type wave functions, with the appropriate change of masses in the Hamiltonian. But I found no expansion length in these functions was adequate enough for approaching the known results obtained using the Born-Oppenheimer approximation, leaving aside to surpass them. The problem remained dormant till Drachman heard from Steve Lundeen about his experimental results on high Rydberg states of H_2 . It is possible to extract accurate properties like quadrupole moment and the parallel and perpendicular polarizabilities of the molecular ion H_2^+ from these results [85,86]. The Born-Oppenheimer results [87] disagreed with the experimental results. We tried to resurrect our old work and tried various extrapolations, but had no success. Drachman came up with an excellent idea: simply raise r_{12} (the interparticle distance between similar particles) to a power close to 30 or so and choose the nonlinear parameter α in $e^{-\alpha r_{12}}$ equal to half of that power of r_{12} in the Hylleraas functions being used. This was a miracle in the sense that nearly six terms in the Hylleraas expansion now were equivalent to hundreds of terms in the earlier expansion! It is easy to understand, after the fact, that now two protons stayed clamped at their respective positions whereas they enjoyed the same freedom as electrons with the usual generalized Hylleraas functions. This was just what was needed to get excellent results without making Born-Oppenheimer like approximations. The expression for polarizability [88] is given by

$$\alpha_1 = \frac{4}{\mu^3(1+\mu)^2} \sum_N \frac{|\langle 0|z_A + z_B|N \rangle|^2}{E_N - E_0} a_0^3, \quad (165)$$

where $z_A = r_A \cdot \hat{\epsilon}$ and $z_B = r_B \cdot \hat{\epsilon}$, ϵ being the direction of the external electric field which can be considered to be in the z direction, r_A and r_B are the distances of the electron from protons A and B, respectively. The reduced mass $\mu = M/(M+1)$. It should be pointed out that we are treating all the particles on an equal footing and we do not refer to any special "molecular" quantum numbers. Thus we are not interested here in the "axial" or "transverse" polarizabilities that appear in the Born-Oppenheimer approximation.

With these modified Hylleraas functions, we obtained ground state energy $E(H_2^+) = -1.194\,277\,909$ Ry, differing by only about 2.2×10^{-7} Ry from the accurate value [89]. We calculate the intermediate P states also using high powers of r_{12} (cf. [88] for details). Our final results for H_2^+ and D_2^+ are given in Table XIV.

Table XIV. Polarizabilities of H_2^+ and D_2^+ obtained in different ways, both theoretically and experimentally. Quantities in parentheses are errors in the last decimal place given.

Method	$\alpha_1(H_2^+)$	$\alpha_1(D_2^+)$
Experiment ^a	3.1681(7)	3.0712(7)
Born-Oppenheimer ^b	3.1713	3.0731
Modified generalized Hylleraas functions	3.1680	3.0671
Finite element ^c	3.1682(4)	3.0714(4)

^aJacobson *et al.* [86]. ^bBishop and Lam [87]. ^cShertzer and Greene [90].

It is obvious that the results for D_2^+ are not as close to the experimental results as in the case of H_2^+ , showing that even the modified wave functions have limitations: as the nuclei get heavier it becomes more difficult to generate a well-enough localized two-nucleus part of the trial wave function. Clearly, the method fails as the nuclei become infinity heavy.

Dr. J. Shertzer discusses in these Proceedings the results obtained by the finite-element method.

Polarizabilities of HD^+

After we had studied the polarizability of the homonuclear molecular ions it should have been simple to extend our methods to the heteronuclear ion HD^+ . Janine Shertzer reminded Drachman that in this case there would be dipole coupling between rotational levels with $J=0$ and $J=1$, which was not possible in the earlier cases because of symmetry. In addition she pointed out that the lowest-lying $J=1$ level is so close to the ground state that one would expect a very high value of polarizability, since the denominator of the second-order perturbation sum would be so small. Drachman and I [91] carried out calculations to see if this prediction was borne out.

The dipole polarizability α_1 is given by the second-order perturbation theory:

$$\alpha_1 = \sum_N \frac{\langle 0|d|N \rangle \langle N|d|0 \rangle}{E_N - E_0} a_0^3. \quad (166)$$

The dipole operator d depends on masses of the nuclei and is given by

$$d = 2 \left[\frac{M_D + 1}{M_T} \mathbf{r}_1 + \frac{M_P + 1}{M_T} \mathbf{r}_2 \right] \cdot \hat{\epsilon}, \quad (167)$$

where the unit vector $\hat{\epsilon}$ is in the direction of the applied electric field, M_P and M_D are the masses of the proton and deuteron nuclei and

$$M_T = M_P + M_D + 1. \quad (168)$$

The calculation of the dipole polarizability of HD^+ is similar to that of H_2^+ and D_2^+ : we treat all three particles on an equal footing and do not refer to any special "molecular" quantum numbers. We use the modified generalized Hylleraas type wave functions, i.e., we use very high powers of n in $r_{12}^n e^{-\alpha r_{12}}$ and α is of the order of $n/2$. The energy eigenvalues using the Rayleigh-Ritz variational

principle are $E_0=-1.195\,795\,889$, using 560 terms, and $E_p=-1.195\,372\,602$ Ry, using 728 terms, for the ground S state and the lowest P state, respectively. These compare well with $E_0=-1.195\,795\,931$ and $E_p=-1.195\,396\,2560$ Ry obtained by Moss [92]. The energies of these two states are so close to each other that they are almost degenerate states of opposite parity. This is the important difference between the homonuclei H_2^+ and D_2^+ , and heteronuclei HD^+ molecules.

The polarizability due to the lowest P term alone in Eq. (166) is $392.0814a_0^3$ and the sum over the remaining intermediate states contributes $\bar{\alpha}_s=3.2076a_0^3$. The total polarizability, $\alpha_1=395.289a_0^3$, is very much larger than might be expected from the results [88] in H_2^+ and D_2^+ . This can be traced to the fact, as indicated above, that there is a coupling between the two lowest S and P states due to their closeness in energy. If we exclude the ground state, we can calculate the polarizability of the lowest P state by summing over all the intermediate S states. We find this result to be $\bar{\alpha}_p=2.03008a_0^3$.

But second-order perturbation theory can only be legitimately carried out if the perturbation is small compared to the spacing of the unperturbed energies, and this condition is hard to satisfy in the present case. If the perturbation is due to a unit charge it must lie further from the ion than about $32a_0$ for the perturbation theory to be valid. What happens for larger fields or smaller distances? Clearly, for these larger fields the opposite parity levels act essentially as degenerate levels, so the techniques of degenerate perturbation theory must be applied. This leads to an energy shift that is linear in the electric field, falling like R^{-2} rather than R^{-4} as we expect for ordinary polarizability. This is usually described as the effect of a permanent dipole moment. We then went on to diagonalize the perturbation matrix in various approximations and were able to give a good description of the energy shift as a function of R .

In observing the Rydberg states of HD , the effective polarizability should be $\bar{\alpha}_s=3.2076a_0^3$, which is close to the polarizabilities of H_2^+ and D_2^+ [88]. With this value, we have calculated energy shifts

$$\Delta_{NL} \equiv -\bar{\alpha}_s \int \Psi_{NL}(\mathbf{R}) \frac{1}{R^4} \Psi_{NL}(\mathbf{R}) d\mathbf{R}, \quad (169)$$

using hydrogenic wave functions. We give these energy shifts Δ_{NL} of a series of Rydberg levels due to the polarizability of the HD^+ ionic core omitting the lowest rotationally excited level in the summation over intermediate states.

Table XV. Energy shifts Δ_{NL} of a series of Rydberg levels.

N	L	$-\Delta_{NL}$ (MHz)
9	4	11501
	5	3943.6
	6	1594.9
	7	720.08
	8	350.41
10	4	8527.4
	5	2951.8
	6	1208.8
	7	554.8
	8	275.89
	9	145.2

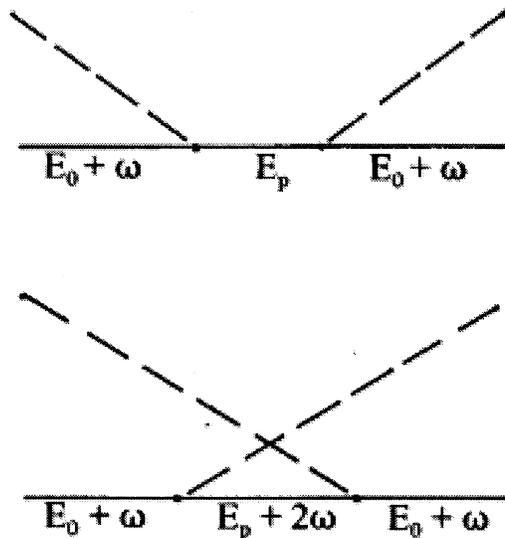


Figure 6: Diagrams symbolizing the nonrelativistic calculation of $\alpha(\omega)$, with energies of each state indicated.

Optical Properties of He Including Relativistic Corrections

An interesting application of polarizabilities is the calculation, which Drachman and I [93] carried out, of the index of refraction n of He from which the Verdet constant V , which measures the rotation of the plane of polarization in the Faraday effect, can be obtained. The rotation θ , measured in degrees, is given by

$$\theta = VBL, \quad (170)$$

where B is the magnetic field and L is the length traversed by light. If the static field is replaced by an oscillating field (an electromagnetic wave), it is possible to define a frequency-dependent polarizability $\alpha(\omega)$ from which the index of refraction can be obtained (cf. Fig 6). The expression for the polarizability is given by

$$\begin{aligned} \alpha(\omega) &= \frac{1}{2} \sum_N \langle 0|Z|N \rangle \langle 0|Z|N \rangle \left[\frac{1}{E_N - (E_0 + \omega)} + \frac{1}{(E_N + 2\omega) - (E_0 + \omega)} \right] \\ &= \sum_N \frac{\langle 0|Z|N \rangle \langle N|Z|0 \rangle (E_N - E_0)}{(E_N - E_0)^2 - \omega^2}, \end{aligned} \quad (171)$$

where $N \equiv p$ and the dipole operator Z is given by

$$Z = 2(z_1 + z_2). \quad (172)$$

We can define a set of "generalized dipole polarizabilities" as follows

$$[\alpha_1, \beta_1, \gamma_1, \delta_1, \epsilon_1, \xi_1, \eta_1] = \sum_N \frac{\langle 0|Z|N \rangle \langle N|Z|0 \rangle}{(E_N - E_0)^{(1,2,3,4,5,6,7)}}. \quad (173)$$

As indicated earlier, we use Hylleraas basis sets for the ground state as well as for pseudostates N and the results for various quantities are given in Table XVI.

Table XVI. Various quantities
for ${}^4\text{He}$.

α_1	1.383 241 01
β_1	0.707 521 493
γ_1	0.385 538 368
δ_1	0.218 735 026
ϵ_1	0.127 538 649
ξ_1	0.075 827 657
η_1	0.045 731 135

The denominator in Eq. (171) can be expanded in powers of $\omega/(E_N - E_0) \leq 0.2$ for wavelengths of visible light:

$$\alpha(\omega) = \alpha_1 + \gamma_1\omega^2 + \epsilon_1\omega^4 + \eta_1\omega^6 + \dots \quad (174)$$

The relativistic corrections are calculated by using the Breit-Pauli relativistic Hamiltonian which has the following form:

$$B = \alpha^2 \left\{ -\frac{1}{4}[\nabla_1^4 + \nabla_2^4] + 2\pi[\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)] + 2\pi\delta(\mathbf{r}_{12}) + \frac{1}{r_{12}}[\nabla_1 \cdot \nabla_2 + \hat{r}_{12} \cdot (\hat{r}_{12} \cdot \nabla_1)\nabla_2] \right\}. \quad (175)$$

This requires a third-order-perturbation theory, with B retained to first order and Z to the second order. Up to ω^4 the expansion corresponding to Eq. (174) gives the following numerical result

$$\Delta\alpha(\omega) = -8.0029 \times 10^{-5} - 8.1516 \times 10^{-6}\omega^2 + 3.006 \times 10^{-7}\omega^4, \quad (176)$$

and the relativistic expression for the frequency-dependent polarizability of helium becomes

$$\alpha_{\text{rel}}(\omega) = 1.383160981 + 0.385530216\omega^2 + 0.12753895\omega^4 + 0.04573114\omega^6. \quad (177)$$

The last term Eq. (177) has not been modified from its nonrelativistic value, since the effect of relativity here would be absolutely negligible. In order to write the above expression in terms wavelength, we use

$$\omega = \frac{4\pi a_0}{\alpha(1 - K/2)\lambda} = \frac{911.39198}{\lambda}, \quad (178)$$

where $K=2.741\,493 \times 10^{-4}$ for ${}^4\text{He}$ and the wavelength is in \AA units. We obtain the expression for polarizability in terms of wavelength in the form:

$$\alpha_{\text{rel}}(\lambda) = 1.383729930 + \frac{3.204546 \times 10^5}{\lambda^2} + \frac{8.822907 \times 10^{10}}{\lambda^4} + \frac{2.624092 \times 10^{16}}{\lambda^6} a_0^3 \quad (179)$$

Optical measurements usually give $n - 1$, where n is close to 1 for helium. The higher-order corrections in the relation between the polarizability (a single atom property) and the index of refraction, due to the effects in the medium, are accounted for by the Lorenz-Lorentz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N_L a_0^3 = 16.67718 \times 10^{-6} \alpha_{\text{rel}}(\lambda) \equiv z \quad (180)$$

where N_L is Loschmid's number. Solving for n to second order in z , we find

$$n - 1 \simeq \frac{3}{2}z + \frac{3z^2}{8} = 34.61527 \times 10^{-6} + \frac{8.016511}{\lambda^2} + \frac{2.207154 \times 10^6}{\lambda^4} + \frac{6.564503 \times 10^{11}}{\lambda^6}. \quad (181)$$

The Verdet constant is given by

$$V = -\frac{e}{2mc^2} \lambda \frac{dn}{d\lambda} = \frac{1.616813 \times 10^7}{\lambda^2} \left[1 + \frac{5.506521 \times 10^5}{\lambda^2} + \frac{2.456618 \times 10^{11}}{\lambda^4} \right] \mu \text{ min/oer cm}, \quad (182)$$

where min refers to rotation. We get from the above equation $V=0.661\ 22 \pm 0.00025$ at $\lambda=5000\text{\AA}$ versus the experimental value 0.637 of Leonard [94], while at $\lambda=8000\text{\AA}$ we get $V=0.254\ 816 \pm 0.000\ 015$ compared with the experimental value 0.246 (all in units of μ min/oer cm). This shows that there is a significant discrepancy here that is larger than the relativistic effects that we have considered. The experimental results do not appear to be very accurate and new measurements are required of the refractive index n of helium to have a better comparison between our theoretical results and measurements.

Another Way to Calculate Lamb Shift

One of the most difficult parts in two-electron Lamb shift calculations is the Bethe logarithm given by

$$\begin{aligned} \ln(K) &= \frac{\sum_n \langle 0|V|n \rangle \langle n|V|0 \rangle (E_n - E_0)^3 \ln(E_n - E_0)}{\sum_n \langle 0|V|n \rangle \langle n|V|0 \rangle (E_n - E_0)^3} \\ &\equiv \frac{N}{D}, \end{aligned} \quad (183)$$

where $|n \rangle$ are $L=1$ eigenstates, both bound and continuum, of the Hamiltonian describing the two-electron system. Instead, we use the pseudostate summation method. The interaction V is given by

$$V = z_1 + z_2 = r_1 \cos\theta_1 + r_2 \cos\theta_2. \quad (184)$$

Having used pseudostates in the polarizability calculations, it should have been easy to calculate $\ln(K)$ given by the above expression in the length form. But the result obtained using either the length, or velocity, or acceleration form never seemed to approach the known results, no matter how large the pseudostate expansion was in the above expression. The basic reasons are the power of $(E_n - E_0)$ which is 3 instead of -1, as in the polarizability expression, and the presence of $\ln(E_n - E_0)$ in the numerator, which makes matters worse. Combined together, the convergence of the results

becomes extremely slow. Out of frustration, I sought Drachman's help. To solve this problem, he came up with several tricks which I prefer to call good insight. We could then obtain results as accurate as available in the literature. I have used a slightly different notation in this section for the pseudostates in order to conform with our published paper [95].

The Denominator

We transform the denominator D in Eq. (183) in a form which does not have an intermediate sum $|n\rangle$ by using the commutation relation

$$\langle n|[H, V]|0\rangle = \langle n|V|0\rangle (E_n - E_0) \quad (185)$$

three times, in order to remove $(E_n - E_0)$:

$$D = \frac{2}{3}(2 + K)^2 \{ \langle 0|[H, (\nabla_1 + \nabla_2)] \cdot (\nabla_1 + \nabla_2)|0\rangle - \langle 0|(\nabla_1 + \nabla_2) \cdot [H, (\nabla_1 + \nabla_2)]|0\rangle \}. \quad (186)$$

Since the potential term in the Hamiltonian does not commute with $\nabla_1 + \nabla_2$, the above expression can be put in the form

$$D_{\text{ex}} = \frac{16\pi Z(1 + K)}{3} \langle 0|\delta(\mathbf{r}_1) + \delta(\mathbf{r}_2)|0\rangle, \quad (187)$$

where closure over the intermediate states $|n\rangle$ has been invoked and Poisson's equation has been used to introduce δ functions. As before, $K = 2/(M + 1)$, where M is the mass of the nucleus in units of the electron mass. The terms of the order K^2 have been dropped; within this error the expression is exact. It does depend on the accuracy of the ground state wave function which consists here of 525 terms. Therefore, the error due to the accuracy of the ground state wave function is negligible.

Table XVII. $\ln(K)$ as a function of γ and Pekeris number Ω_p .

Ω_p	γ	D_{acc}	N_{acc}	$\ln(K)$
3	3.644 529	94.114 569	301.053 261	3.198 796
4	4.080 394	101.216 416	346.195 202	3.420 346
5	4.425 096	104.957 668	373.513 205	3.558 703
6	4.849 542	108.413 460	399.676 322	3.686 593
7	5.179 484	110.403 345	416.057 508	3.768 523
8	5.588 226	112.320 411	432.319 315	3.848 983
9	5.888 226	113.508 976	442.840 189	3.901 367
10	6.305 080	114.676 534	453.744 402	3.956 373
11	6.623 156	115.446 146	461.125 678	3.994 293
12	7.004 813	116.207 693	468.586 094	4.032 316
13	7.3	116.735 692	473.876 067	4.059393

Because of the $\ln(E_n - E_0)$ term, it is not possible to reduce N to a similar form. However, we expect the convergence of pseudostates will be similar for N and D . We use the commutation relation [Eq. (185)] twice for each matrix element of Eq. (183) to obtain the acceleration form

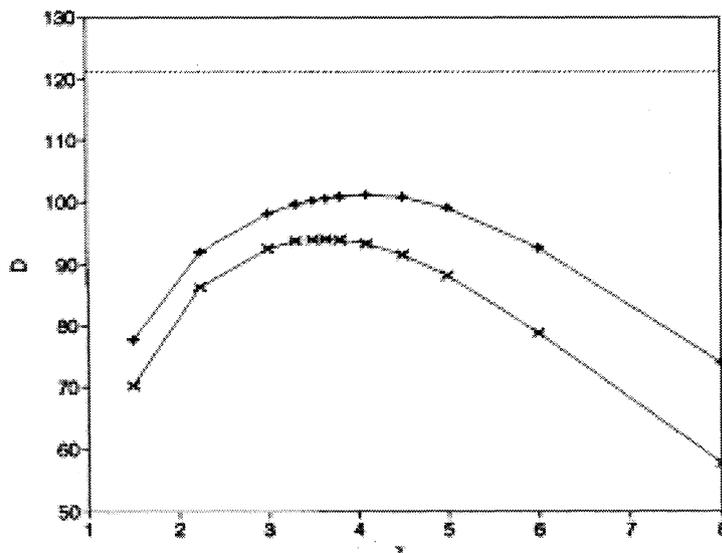


Figure 7: Behavior of D_{acc} for helium as a function of the nonlinear parameter γ . The crosses are for $\Omega_p=3$, and the plus signs are for $\Omega=4$. The dotted line is the "exact" value, obtained from Eq. (187).

$$D_{acc} = -8Z^2(1+K) \sum_n \frac{\langle 0|U|n \rangle \langle n|U|0 \rangle}{E_0 - E_n}, \quad (188)$$

where

$$U = \frac{\cos\theta_1}{r_1^2} + \frac{\cos\theta_2}{r_2^2}. \quad (189)$$

This expression for D_{acc} looks like the second-order energy shift induced by the potential U , and it has a variational bound [95]. We can, therefore, choose the nonlinear parameter γ in the pseudostates to maximize D_{acc} in Eq. (188) (cf. Fig. 7).

As the number of $|n \rangle$ is increased the D_{acc} approaches D_{ex} which for He from Eq. (187) is 121.335 143. We calculate N for the same γ and the same number of $|n \rangle$ as for D_{acc} . We give values of $\ln(K)$ as a function of the Pekeris number Ω_p in Table XVII.

Extending The Upper Limit

We assume that the contribution of each term in the pseudostate summation is exact and the remaining error in the total is due to the fact that the sum does not extend to infinity. We use the method of Dalgarno and Stewart [96] to account for the remainder of the sums beyond the highest pseudoenergy. For high energies they used the following simplified form:

$$\Psi_{n,\mathbf{k}}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{2\pi} \left(\frac{k}{2}\right)^{1/2} [u_n(\mathbf{r}_1)e^{i\mathbf{k}\cdot\mathbf{r}_2} + u_n(\mathbf{r}_2)e^{i\mathbf{k}\cdot\mathbf{r}_1}], \quad (190)$$

to represent the singly ionized states in the expression that replaces the discrete one in Eq. (188):

$$F_n(\epsilon) = \frac{16Z^2(1+K)}{3(I_n + \epsilon)} \left| \langle \Psi_0 | \left[\frac{\mathbf{r}_1}{r_1^3} + \frac{\mathbf{r}_2}{r_2^3} \right] | \Psi_{n,\mathbf{k}} \rangle \right|^2. \quad (191)$$

Here $\epsilon = k^2$, I_n is the ionization-excitation potential of two-electron systems, and u_n is the wave function of the one-electron system left after single ionization. Without loss of accuracy, we fitted $F_n(\epsilon)$ to the form $[A_n + (B_n/k)\tan^{-1}(C_n/k)]\epsilon^{-3/2}$ and included s states up to $n=4$. Higher states were included approximately by an expression falling like $1/n^4$. We adjust ϵ_0 so that

$$D_{ex} = D_{acc} + \int_{\epsilon_0}^{\infty} d\epsilon \sum_n F_n(\epsilon). \quad (192)$$

The critical step is now to correct N using the same value of ϵ_0 as for the denominator, modifying the integral by the inclusion of the appropriate logarithmic factor. In Table XVIII, to obtain the exact value of the denominator we give the required value of ϵ_0 , the corrected value of the numerator and the improved value of $\ln(K)$; the convergence with Ω_p is significantly improved.

Table XVIII. The ϵ_0 , corrected values of N_{corr} , and $\ln(K)$.

Ω_p	ϵ_0	N_{corr}	$\ln(K)$
3	361.0613	520.267 518	4.287 855
4	724.0096	521.248 382	4.295 939
5	1143.441	523.110 217	4.311 284
6	1912.977	524.085 779	4.319 324
7	2734.433	525.086 045	4.327 568
8	4108.808	525.799 439	4.333 447
9	5524.324	526.334 777	4.337 859
10	7729.503	526.911 785	4.342 614
11	9964.945	527.307 234	4.345 874
12	13 253.52	527.650 177	4.348 700
13	16 564.86	527.870 611	4.350 517

Extrapolation and Results

We extrapolate our results by using the deviation ΔD of the denominator from its exact value:

$$\Delta D = D_{ex} - D_{acc} \quad (193)$$

This quantity approaches zero as Ω_p increases. We plot the uncorrected and corrected $\ln(K)$ (cf. Fig. 8).

The slope of the line fitted to the corrected points is 12 times smaller than the uncorrected slope, indicating the improved convergence we expected. The extrapolated result for helium is $\ln(K)=4.367\ 58(46)$.

In Table XIX we show the values of $\ln(K)$, obtained by this method, for a range of atomic numbers Z and compare them with those obtained from the approximate expression of Goldman and Drake [97]. Their approximate expression has been obtained using an expansion in $1/Z$:

$$\ln(K) = \ln[19.7692669(Z - 0.00615)^2]. \quad (194)$$

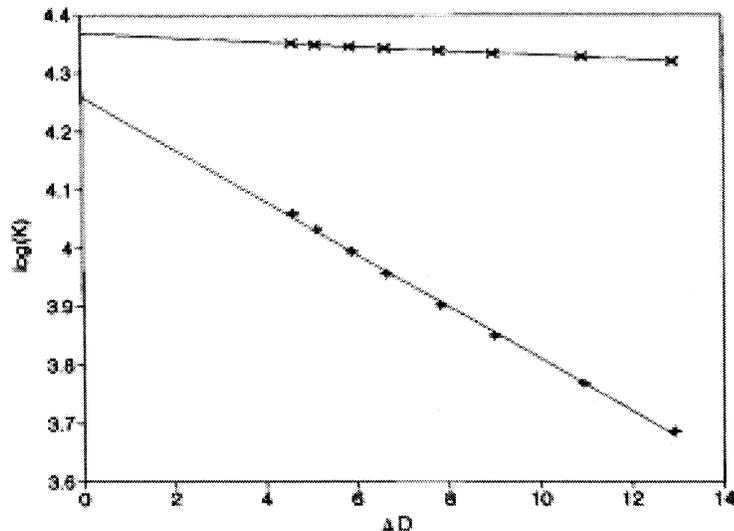


Figure 8: $\ln(K)$ for helium as a function of ΔD . The plus signs show the uncorrected values, using the data from Table XVII, and the crosses are the corrected values from Table XVIII. Linear fits have been made in both cases, and the improved convergence of the corrected values is clear.

Table XIX. Results for a series of two-electron systems.

System	Z	$\ln(K)$	$\ln(K)^a$
He	2	4.367 578	4.364 263
Li ⁺	3	5.177 763	5.177 249
Be ⁺²	4	5.753 615	5.753 640
Ne ⁺⁸	10	7.586 072	7.588 068

^aFrom Eq. (14) of Ref. [97] which is the same as Eq. (194) given above.

A good fit to our results is the form:

$$\ln(K) = \ln[19.705541(Z + 1.35 \times 10^{-5})^2]. \quad (195)$$

The present results may represent the two-electron ground state Bethe logarithm well over the range $2 \leq Z \leq 10$.

$\ln(K)$ for Atomic Hydrogen

It is an obviously interesting question to see how well the above method works for the simpler and better known one-electron (atomic hydrogen) case. Here the ground state wave function is known exactly and the pseudostates are of a simple one-electron form:

$$\Psi_0 = \frac{e^{-r}}{\pi^{1/2}}, \quad \Psi_n = e^{-\gamma r} P_1(\theta) \sum_{j=1}^{\Omega_p} C_j r^j. \quad (196)$$

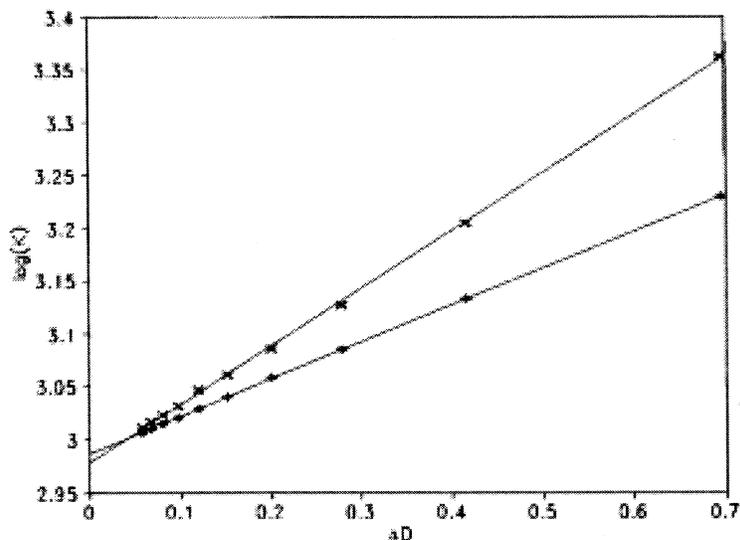


Figure 9: $\ln(K)$ for hydrogen as a function of ΔD . The alternating convergence pattern discussed in the text leads to two distinct lines: crosses are for even values and plus signs are for odd values of Ω_p .

The denominator can be evaluated exactly: $D=16/3$. All other steps described above can be applied to the one-electron system.

In Fig. 9 we show the unexpected results. In place of the linear relation found for two-electron systems, we obtain an alternating convergence pattern. As Ω_p increases from an odd value to the next even value the numerator increases significantly while the denominator remains unchanged to 7 or 8 significant figures. With the next increase in Ω_p the increase in D resumes. This effect produces two distinct lines. We were able to carry the calculations up to $\Omega_p=22$, at which point $\Delta D=0.057$. The extrapolations to $\Delta D=0$ give $\ln(K)=2.987\ 125$ (from odd values of Ω_p) and $\ln(K)=2.978\ 329$ (from even values). Combining the two results we can report a "best" value of $\ln(K)=2.9827 \pm 0.0044$ which should be compared to the accurate value of Haywood and Morgan III [98] $\ln(K)=2.984\ 129$; our generous error does include this value.

We have not been able to understand this irregular convergence and this remains an interesting unanswered question.

Rydberg States of Li

Traditionally, eigenvalues and eigenfunctions are calculated by the use of the Rayleigh-Ritz variational principle. This procedure has been carried out for states with high quantum numbers, N and L , as well [99]. The disadvantage is eigenvalues of all the states below the state of interest have to be calculated. Drachman realized that when N is large, say 10, the outer electron is so far away [$100 a_0$ compared to a_0 for the core electrons] from the spherically symmetric core that it does not have much electron-electron correlations, the type taken into account by the Hylleraas functions, with the core electrons. Even the exchange is not important, and most of the of correlations can be taken into account by considering only the long-range interactions. On this basis, he developed

a formalism [100] to calculate energies of states of interest only, using the Feshbach projection operator technique. Since the exchange can be ignored Eq. (71) simplifies to

$$P = P_1 = |\phi_0 \rangle \langle \phi_0|. \quad (197)$$

The formalism is rather complicated and I give the final result for the effective potential seen by the outer electron at a distance x from the nucleus:

$$U(x) = -\frac{\alpha_1}{x^4} + \frac{6q\beta_1 - \alpha_2}{x^6} + \frac{\delta + 16q^2\gamma_1/5}{x^7} + \frac{-\alpha_3 + 15q\beta_2 - \epsilon + \alpha_1\beta_1 - 72q^2\gamma_1[1 + L(L+1)/10]}{x^8} \dots \quad (198)$$

I alluded to this form in Eq. (155), where I indicated the importance of polarizabilities in the Rydberg states. The core coefficients are described below:

$$S_{k,i} \equiv x^{2i+2} \sum_n \frac{\langle 0|V_i|n \rangle \langle n|V_i|0 \rangle}{(E_n - E_0)^k}. \quad (199)$$

Here, as mentioned before, $\alpha_i = S_{1,i}$, $\beta_i = S_{2,i}$, and $\gamma_i = S_{3,i}$. The third-order polarizability has the form:

$$\delta \equiv x^7 \sum_{n,m} \frac{\langle 0|V_i|n \rangle \langle n|V_j|m \rangle \langle m|V_k|0 \rangle}{(E_n - E_0)(E_m - E_0)}. \quad (200)$$

The values that (ijk) can take are all the permutations of [112]. Finally, the fourth-order hyperpolarizability involving the dipole terms has the form:

$$\epsilon \equiv x^8 \sum_{n,m,p} \frac{\langle 0|V_1|n \rangle \langle n|V_1|m \rangle \langle m|V_1|p \rangle \langle p|V_1|0 \rangle}{(E_n - E_0)(E_m - E_0)(E_p - E_0)}. \quad (201)$$

Drachman [100] developed the formalism for helium atoms and showed that he could obtain the same result as Drake [99] did for the eigenvalues, e.g., $N=10$ and $L=6$ his result $E=-105.82980 \pm 0.00014$ compares very well with -105.829683489 MHz of Drake (cf. Table III of Ref. [100]).

Up to now I have not given the interaction potentials V_1 , V_2 , and V_3 . We are now interested in the Rydberg states of Li where the spherical core is He-like and therefore, I give below expressions [101] for three-electron systems:

$$V_1 = \frac{2q^2w}{x^2} \left[\frac{2 + (Z-1)K}{2+K} \right] P_1(\hat{w} \cdot \hat{x}), \quad (202)$$

$$V_2 = \frac{2q^3}{x^3} \left[r_1^2 P_2(\hat{r}_1 \cdot \hat{x}) + r_2^2 P_2(\hat{r}_2 \cdot \hat{x}) - \frac{4K + ZK^2}{(2+K)^2} w^2 P_2(\hat{w} \cdot \hat{x}) \right], \quad (203)$$

$$V_3 = \frac{2q^4}{x^4} \left[\frac{2-K}{2+K} [r_1^3 P_3(\hat{r}_1 \cdot \hat{x}) + r_2^3 P_3(\hat{r}_2 \cdot \hat{x})] - \frac{4K - 2K^2 - ZK^3}{(2+K)^3} w^3 P_3(\hat{w} \cdot \hat{x}) \right], \quad (204)$$

where $\mathbf{w} = \mathbf{r}_1 + \mathbf{r}_2$ and $q \simeq 1 + K^2/2$. In Table XX we give the various quantities for ${}^7\text{Li}^+$ and ${}^6\text{Li}^+$, which have been calculated by using the appropriate Hylleraas type wavefunctions for the ground state and intermediate pseudostates of angular momentum $L=1, 2$, and 3 . Again we use the method of pseudostate summation.

Table XX. Best values of the core parameters used in constructing the effective potential. The upper entry is for ${}^6\text{Li}$ and the lower one is for ${}^7\text{Li}$.

α_1	β_1	γ_1	α_2
0.192 490 771	0.035 286 879	0.006 806 377	0.113 825 934
0.192 485 410	0.035 286 017	0.006 806 227	0.113 834 685
β_2	γ_2	δ	ϵ
0.016 670 328	0.168 351 237	0.121 337 559	0.027 039 600
0.016 671 511	0.168 362 339	0.121 345 411	0.027 038 073

From the core parameters of Table XX the effective potential of Eq. (198) can be constructed explicitly. Numerically, this potential is

$$U(x) = -\frac{0.19248540}{x^4} + \frac{0.097881}{x^6} + \frac{0.143125}{x^7} - \frac{0.428584 + 0.049005L(L+1)}{x^8} \quad (205)$$

for the case of ${}^7\text{Li}$. We use the following expression for the energy shift $\Delta(NL)$ away from the unperturbed energy $-R/N^2$

$$\Delta(NL) = R \left[(U_4 + U_6) + \frac{1}{2}[U_7 + U_8] \pm \frac{1}{2}[U_7 + U_8] \right], \quad (206)$$

where the reduced Rydberg $R=3.289\,584\,678 \times 10^9$ MHz for ${}^7\text{Li}$, and where U_k is the expectation value of that term in $U(x)$ which goes like x^{-k} . Since the unperturbed wavefunction of the outer electron is purely hydrogenic, these expectation values can be evaluated analytically and exactly. Some results are given in Table XXI for $N=10$ and various values of L (cf. Table II of Ref. [101] for values for other N and L).

Table XXI. Level shifts (in MHz) for ${}^7\text{Li}$ for $N=10$ due to the effective potential terms U_k . The total and error are obtained as described in Eq. (206).

L	U_4	U_6	$U_7 + U_8$	Total	Error
4	-511.674	2.332	-0.229	-509.457	0.115
5	-177.1181	0.3007	-0.0022	-176.8185	0.0011
6	-72.5341	0.0541	0.0005	-72.4798	0.0003
7	-33.29026	0.01190	0.00014	-33.27829	0.00007
8	-16.554171	0.002929	0.000033	-16.51226	0.000017
9	-8.712722	0.000738	0.000007	-8.711981	0.000004

Since U_8 has been included, α_1/x^4 should also be included to the second order. That is

$$\Delta_2 = \sum_N' \frac{\langle NL|\alpha_1/x^4|N'L \rangle \langle N'L|\alpha_1/x^4|NL \rangle}{E_N - E_{N'}} \quad (207)$$

Here the intermediate states $N'L$ are the hydrogenic states of the outer electron. This quantity has been calculated for He [100], Δ_2 for ${}^7\text{Li}$ can be obtained by scaling the results for He; Δ_2 being proportional to α_1^2 . The results, given in Table XXII, are again shown only for the $N=10$ and various L . The large relativistic correction due to increase in mass with velocity has been discussed by Bethe and Salpeter [102] and some details are given in [101], as well. We obtained the following expression for the leading relativistic correction:

$$\Delta_{\text{rel}} = \frac{\alpha^2 R}{N^3} \left[\frac{3}{4N} \left[1 - \frac{K}{6} \right] - \frac{2}{2L+1} \right], \quad (208)$$

which is accurate up to order K^2 . Again some results are given in Table XXII.

Table XXII. Second-order corrections, leading relativistic corrections, and the final total shifts for ${}^7\text{Li}$ in MHz for $N=10$.

L	Δ_2	Δ_{rel}	Total+ Δ_2 + Δ_{rel}
4	-0.097	-25.790	-535.343±0.115
5	-0.0090	-18.7122	-195.5397±0.0011
6	-0.0012	-13.8122	-86.2932±0.0003
7	-0.0022	-10.218 88	-43.497 39±0.000 07
8	-0.000 046	-7.471 035	-24.022 31±0.000 02
9	-0.000 011	-5.301 687	-14.013 679±0.000 0004

The fine-structure splitting for the $N=10$ manifold are shown in Table XXIII, where they are compared with the accurate measurements of Rothery *et al.* [103].

Table XXIII. Fine-structure splitting for the $N=10$ manifold of ${}^7\text{Li}$.

Interval	Energy shift(MHz)	Experiment [103] (MHz)
10G-10H	339.80±0.011	339.7186±0.0031
10H-10I	109.246 6±0.001 1	109.2140±0.0047
10I-10K	42.795 8±0.000 3	
10K-10L	19.475 08±0.000 07	
10L-10M	10.008 63±0.000 02	

Considering the accuracy of the measurements, the agreement between theory and experiment is not very good. Drachman and I [104] extended our work [101] to include corrections to the third order to improve the agreement.

Relativistic Correction to the Polarization Potential

We wish to compute a correction to the energy shift of a Rydberg level due to the Breit-Pauli relativistic Hamiltonian of order α^2 . Thus we must carry out a third-order perturbation calculation which has the form

$$V_3(x) = \sum_{n,m} \frac{\langle 0|h|n \rangle \langle n|h|m \rangle \langle m|h|0 \rangle}{(E_0 - E_n)(E_0 - E_m)} - \sum_n \frac{\langle 0|h|n \rangle \langle n|h|0 \rangle}{(E_0 - E_n)^2} \langle 0|h|0 \rangle, \quad (209)$$

where $h=H_{\text{dip}} + H_{\text{BP}}$. The expression for the Breit-Pauli Hamiltonian $H_{\text{BP}} \equiv B$ has been given in Eq. (175) and

$$H_{\text{dip}} = \frac{2}{x^2}(\mathbf{r}_1 + \mathbf{r}_2) \cdot \hat{\mathbf{x}}. \quad (210)$$

Keeping terms to order α^2 results in the following:

$$\begin{aligned} V_3^{\alpha^2} &= \sum_{n,m} \left[\frac{\langle 0|H_{\text{dip}}|n\rangle \langle n|H_{\text{BP}}|m\rangle \langle m|H_{\text{dip}}|0\rangle}{(E_0 - E_n)(E_0 - E_m)} + 2 \frac{\langle 0|H_{\text{dip}}|n\rangle \langle n|H_{\text{dip}}|m\rangle \langle m|H_{\text{BP}}|0\rangle}{(E_0 - E_n)(E_0 - E_m)} \right] \\ &\quad - \sum_n \frac{\langle 0|H_{\text{dip}}|n\rangle \langle n|H_{\text{dip}}|0\rangle}{(E_0 - E_n)^2} \langle 0|H_{\text{BP}}|0\rangle \\ &= -\frac{\Delta\alpha_1}{x^4}, \end{aligned} \quad (211)$$

where we have taken account of the facts that the ground state has angular momentum $L=0$, the excited states n, m are $L=0$ or 1, and H_{BP} is rotationally invariant. Our best-converged result, obtained with 161 terms with $L=0$ and 165 terms with $L=1$ is $\Delta\alpha_1 = -4.518 \times 10^{-5}$.

Retardation Corrections

As indicated earlier, the Rydberg electron is at a distance from the nucleus much greater compared to the radius of the core. When the distance is greater than $137a_0$, the interaction is no longer purely Coulomb in character. This is because the delay due to the finite light propagation time between the core and the outer electron is comparable to the characteristic time $t = a_0/v$. This retardation (or Casimir effect) brings in a new type of term [105] in the effective potential acting on the Rydberg electron that falls off like x^{-5} . Au, Feinberg, and Sucher [106] have given the following expressions for the modification of the effective potential producing the energy shift in the state ($1s^2NL$):

$$\Delta_{\text{Ret}}^{NL} = \frac{16}{\pi} \sum_n \frac{|\langle n|z_1 + z_2|0\rangle|^2}{(E_n - E_0)^2} I_n, \quad (212)$$

$$\begin{aligned} I_n &= \int_0^\infty \frac{dt}{(t^2 + 1)} \int_0^\infty \frac{dx}{x^6} R_{NL}^2(x) e^{-2z_n t} [3 - 5z_n^2 + z_n^4 + (6z_n - 2z_n^3)t] \\ &\quad + \int_0^\infty \frac{dx}{x^6} R_{NL}^2(x) \left[6z_n - \frac{z_n^3}{2} - \frac{3\pi}{2} \right], \end{aligned} \quad (213)$$

where $z_n = \frac{1}{2}\alpha x(E_n - E_0)$. The evaluation of this correction is rather complicated. Nevertheless, we have evaluated the retardation corrections from $N=5$ to $N=21$. We give results for the $N=10$ manifold only in Table XXIV.

Table XXIV. Retardation corrections for lithium in MHz for $N=10$ manifold.					
$L=9$	$L=8$	$L=7$	$L=6$	$L=5$	$L=4$
0.000646286	0.00142682	0.00325464	0.00790948	0.0212477	0.0653658

Lamb-Shift Corrections

Since we are interested in the L -dependent fine-structure splitting of the Rydberg levels only the *change* in the Lamb shift of the two-electron core due its interaction with the outer electron needs to be calculated. The main parts of the Lamb shift (mass renormalization, vacuum polarization, and radiative corrections to the magnetic moment) can be written in terms of $(\langle \delta(\mathbf{r}_1) \rangle + \langle \delta(\mathbf{r}_2) \rangle)$, and it is necessary to calculate the dependence of these δ functions on the state of the outer electron. Following Goldman and Drake [107] we can write the expression for the two-electron Lamb shift as

$$\Delta_{\text{Lamb}}^{NL} = \frac{8}{3} Z\alpha^2 \left[-2\ln\alpha + \frac{19}{30} - \ln K \right] (\langle \delta(\mathbf{r}_1) \rangle + \langle \delta(\mathbf{r}_2) \rangle). \quad (214)$$

Here the δ functions refer to the two core electrons but are influenced by the outer electron. This correction is proportional to the expectation value of $1/x^4$ and behaves like another correction to the dipole polarizability of the two-electron core. We can write the relativistic corrections as

$$\Delta_{NL} = [1.486 \times 10^5 - 3.103 \times 10^4] \left\langle \frac{1}{x^4} \right\rangle_{NL} + \Delta_{\text{Ret}}^{NL}, \quad (215)$$

where the quantities in the square bracket are the coefficients (in MHz) of the relativistic polarizability and Lamb-shift corrections, respectively. In Table XXV we show the three types of corrections for the experimentally interesting $N=10$ and their total in MHz.

Table XXV. Relativistic, polarizability, retardation, Lamb shift corrections and the total uncorrected interval from Table XXII, in MHz, for $N=10$ manifold.

L	Uncorrected shift	Relativistic polarizability	Retardation	Lamb shift	Total
4	-535.343±0.115	0.1201	0.0654	-0.0252	-535.183±0.115
5	-195.5397±0.0011	0.0416	0.0212	-0.0087	-195.486±0.0011
6	-86.2932±0.0003	0.0170	0.0079	-0.0036	-86.2719±0.0003
7	-43.49739±0.00007	0.0078	0.0033	-0.0016	-43.4879±0.0001
8	-24.02231±0.00002	0.0039	0.0014	-0.0008	-24.0178
9	-14.013679±0.000004	0.0020	0.0006	-0.0004	-14.0115

Finally, in Table XXVI we compare the experimental fine-structure intervals for lithium [103] with the theoretical totals including the uncorrected values and the three small corrections. It is clear that there is better agreement when the small corrections are included. However, higher-order corrections and more measurements seem to be warranted.

Table XXVI. Comparison of level differences for lithium, in MHz, between theory and experiment [103].

Interval	Experiment-Theory	Standard deviation
10G-10H	0.02	0.11
10H-10I	0.0003	0.0048

We [108] have carried out a similar calculation for CIV, O VI, and Ne VIII. But at present there are no measurements accurate enough to compare with our calculations.

Even though there are other interesting topics on which Dr. Drachman and I have worked on together, I stop here. Instead, I mention below two more topics: one with others and one by himself.

Positronium-hydrogen scattering resonances

Drachman once tried to insert the statement "Nobody likes a smooth cross-section" in an article on resonances, but the referee vetoed it. Nevertheless, there is much more interest in scattering resonances than in bland nonresonant behavior. The Ps-H system is rich in interesting physics: There is one particle-stable state called positronium hydride [PsH] with an energy of about 1 eV below the free Ps+H threshold. Using both the stabilization method and the complex rotation method Drachman and Houston [109] found an s-wave resonance in elastic Ps-H scattering at about 4.5 eV.

Since interesting physics usually emerges from the analysis of resonances, it was of interest to understand the mechanism producing this resonance. At first, it was thought that it was due to some threshold process like that producing resonances in electron-hydrogen scattering below the $n=2$ threshold, but the position obtained was not close enough to a threshold to make this plausible. The best explanation describes it as a Feshbach resonance [110] in which the closed-channel part of the scattering function is the re-arranged system e^+H^- , corresponding to perturbed hydrogenic bound states. Because of the long-range Coulomb potential between the positron and the negative hydrogen ion one can predict that there should be an infinite series of resonances, of which the one found by Houston and Drachman [109] is just the first. Since the hydrogen ion exists only in the singlet spin state these resonances should not occur in the triplet state. No reliable calculation has found triplet resonances.

There are more subtleties in this system, including some problems with the low-lying resonances expected for $L > 0$ [111] and these have been examined very recently by De Rienzi and Drachman [112,113]. More about this interesting system can be found in the presentation by Dr. H. R. J. Walters in this volume.

Hyperfine Splitting in Muonic Helium

Huang and Hughes [114] calculated the Fermi contact term which yields the hyperfine splitting of the ground state of the muonic helium system ($\alpha^{++}\mu^-e^-$) by using a Hylleraas expansion. They required hundreds of terms in the expansion because of the slow convergence. Drachman [115] noticed that the first term in this expansion gave 99.4% of the contribution, suspecting that a perturbative treatment could be an appropriate way of calculating the Fermi contact term. The large ratio of muonic mass to electron mass suggests an adiabatic Born-Oppenheimer approximation.

The nonrelativistic Hamiltonian of this system is

$$H = -\frac{1}{M}\nabla_x^2 - \frac{1}{m}\nabla_r^2 - \frac{4}{x} - \frac{4}{r} + \frac{2}{|\mathbf{x} - \mathbf{r}|}, \quad (216)$$

\mathbf{x} and \mathbf{r} are the coordinates of the muon and electron, respectively, relative to the nucleus. The reduced masses are $M=201.069$ and $m=0.999863$ in units of m_e . The hyperfine splitting is given by

$$\Delta\nu = K \int d\mathbf{x}d\mathbf{r}\overline{\Psi^2}(\mathbf{x}, \mathbf{r})\delta(\mathbf{x} - \mathbf{r}), \quad (217)$$

where Ψ is the ground state eigenfunction of H , and $K = 14196.11$ MHz. In the Born-oppenheimer method, two of the particles are held fixed while we solve for the wave function of the other particle. We hold the muon (\mathbf{x}) fixed and solve for $\psi(\mathbf{r})$ of the electron with \mathbf{x} as a parameter

$$\left(-\frac{1}{m}\nabla_r^2 - \frac{2}{r} + V(\mathbf{x}, \mathbf{r}) - E_x\right)\psi_{\mathbf{x}}(\mathbf{r}) = 0, \quad (218)$$

where $V(\mathbf{x}, \mathbf{r}) = -\frac{2}{r} + \frac{2}{|\mathbf{x}-\mathbf{r}|}$. As indicated in Eq. (106), the solution of Eq. (218) can be written as

$$\psi_{\mathbf{x}}(\mathbf{r}) = \psi_0(\mathbf{r})[1 + G(\mathbf{x}, \mathbf{r})], \quad (219)$$

where

$$\psi_0(\mathbf{r}) = \left(\frac{m^3}{\pi}\right)^{1/2} e^{-mr}, \quad (220)$$

satisfies the Coulomb problem and G is due to the adiabatic perturbation $V(\mathbf{x}, \mathbf{r})$. At this point, Drachman expands G in a perturbation series in V and its first order satisfies the equation (108)

$$\frac{1}{m}\nabla_r^2 G_1 - 2\frac{\partial G_1}{\partial r} = V - \langle V \rangle, \quad (221)$$

where

$$\langle V \rangle = \int d\mathbf{r}\psi_{\mathbf{x}}(\mathbf{r})V\psi_{\mathbf{x}}(\mathbf{r}) = 2[1/x - m - e^{-2mx}(1/x + m)] \quad (222)$$

is the expectation value of V . Dalgarno and Lynn [51] have solved an equation similar to Eq. (221) but for an electron in the field of two fixed positive charges. Using their solution with suitable modification, Drachman obtains

$$G_1(\mathbf{x}, \mathbf{x}) = \frac{5}{2} - x - (2/x)E_1(2x) - (1/x+1)\ln(2\gamma x) - e^{-2x}\left\{\frac{1}{2} + 2x + (1/x+1)[2\ln(2\gamma x) - \text{Ei}(2x)]\right\}, \quad (223)$$

where E_1 is an exponential integral and Ei is defined in Eq. (114). Now we can solve Eq. (218) for E_x to obtain $E_x = -m + \langle V \rangle + \langle VG_1 \rangle$ and determine the muonic wave function by solving the equation

$$\left[-\frac{1}{M}\nabla_x^2 - \frac{4}{x} - E_x - E\right]\Phi(\mathbf{x}) = 0. \quad (224)$$

Since muon is close to the nucleus due to its large mass, only small values of x are significant and the Coulomb term dominates. Therefore ignoring the third term, the solution is hydrogenic:

$$\Phi(\mathbf{x}) = (8M^3/\pi)^{1/2}e^{-2Mx}. \quad (225)$$

Finally, letting $\Psi(\mathbf{x}, \mathbf{r}) \equiv \Phi(\mathbf{x})\psi_{\mathbf{x}}(\mathbf{r})$, Eq. (217) can be written explicitly as

$$\Delta\nu \approx \frac{32K}{\pi}(Mm)^3 \int_0^\infty dx x^2 e^{-x/a} [1 + 2G_1(m\mathbf{x}, m\mathbf{x})], \quad (226)$$

where $a \equiv [4M + 2m]^{-1} = 1.24 \times 10^{-3}$, and the term quadratic in G_1 has been dropped for consistency, since it is of second order in V .

Expanding G_1 and retaining only the linear term in x , we obtain

$$\begin{aligned} \Delta\nu &\approx (32K/\pi)(mM)^3(2a^2 - 12ma^4) \\ &= (4483.38 - 33.36) \text{ MHz} \\ &= 4450.02 \text{ MHz}. \end{aligned} \quad (227)$$

The quadratic term in G_1 contributes 0.689 MHz, while the cubic term is -0.005 MHz. Taking half of the quadratic term as an error, the final result is thus $\Delta\nu=4450.4\pm 0.4$ MHz. This agrees with the result of Huang and Hughes [114] and is also close to the result obtained by Lakdawala and Mohr [117].

This is an excellent example of good physics where a rather complicated problem has been reduced by Dr. Drachman to a relatively simple problem by realizing that the muon is so close to the nucleus that it acts as a hydrogenic system and the rest of the problem is amenable to an adiabatic perturbation treatment, where already some available results could be used gainfully to obtain fairly accurate results. Understanding the intricacies of a problem and solving it in a simple way has been the hallmark of Dr. Drachman's research work throughout.

I wish to thank Keith Feggans for retrieving figures, given in this article, from various published papers.

REFERENCES

1. P. M. Morse and W. P. Allis, Phys. Rev. **44**, 269 (1933).
2. A. Temkin, Phys. Rev. **107**, 1004 (1957).
3. A. Temkin, Phys. Rev. **116**, 358 (1959).
4. R. M. Sternheimer, Phys. Rev. **96**, 951 (1954).
5. A. Temkin and J. C. Lamkin, Phys. Rev. **121**, 788 (1961).
6. I. H. Sloan, Proc. Roy. Soc. **281**, 151 (1964).
7. C. Schwartz, Phys. Rev. **124**, 1468 (1961).
8. R. L. Armstead, Phys. Rev. A **171**, 91 (1968).

9. R. J. Drachman and A. Temkin, "Polarized Orbital Approximations," Case studies in atomic collision physics II, ed. by E. W. McDaniel and M. R. C. McDowell, 1972, pp. 401-481.
10. L. Rosenberg, L. Spruch, And T. F. O'Malley, Phys. Rev. **119**, 164 (1960).
11. A. Temkin, Phys. Rev. Lett. **6**, 354 (1961).
12. G. Breit, Phys. Rev. **35**, 569 (1930).
13. E. A. Hylleraas, Z. Physik **48**, 469 (1928); **54**, 347 (1929).
14. A. K. Bhatia and A. Temkin, Rev. Mod. Phys. **36**, 1050 (1964).
15. A. K. Bhatia and A. Temkin, Phys. Rev. **137**, A1335 (1965).
16. H. Feshbach, Ann. Phys. (N.Y.) **19**, 287 (1962).
17. T. F. O'Malley and S. Geltman, Phys. Rev. **137**, A1344 (1965).
18. A. K. Bhatia, A. Temkin, and J. F. Perkins, Phys. Rev. **153**, 177 (1967).
19. A. K. Bhatia and A. Temkin, Phys. Rev. A **64**, 032709 (2001).
20. A. K. Bhatia, Phys. Rev. A **66**, 064702 (2002).
21. Y. Hahn, T. F. O'Malley and L. Spruch, Phys. Rev. **128**, 932 (1962).
22. A. K. Bhatia, Phys. Rev. A **69**, 032714 (2004).
23. A. K. Bhatia, Phys. Rev. A **73**, 012705 (2006).
24. Y. K. Ho, A. K. Bhatia, and A. Temkin, Phys. Rev. A **15**, 1423 (1977).
25. A. K. Bhatia and A. Temkin, Phys. Rev. A **29**, 1859 (1984).
26. R. P. Madden and Codling, Astrophys. J. **141**, 364 (1965).
27. L. Sanche and P. Barrow, Phys. Rev. Lett. **29**, 1639 (1972).
28. H. Morgan and D. Ederer, Phys. Rev. A **29**, 1901 (1984).
29. A. Temkin and A. K. Bhatia, Phys. Rev. A **31**, 1259 (1985).
30. A. Temkin and A. K. Bhatia, "Projection and Quasi-Projection Operators for Electron Impact Resonances on Many-Electron Atomic Targets," Autoionization: Recent Developments and Applications, ed. by A. Temkin, 1985, pp. 35-70.
31. A. Temkin, A. K. Bhatia, and J. N. Bardsley, Phys. Rev. A **5**, 1663 (1972).
32. G. J. Schulz, Phys. Rev. Lett. **10**, 104 (1963).
33. C. Kuyatt, J. A. Simpson, and S. Mielczarek, Phys. Rev. **138**, A385 (1965).
34. A. Berk, A. K. Bhatia, B. R. Junker, and A. Temkin, Phys. Rev. A **34**, 4591 (1986).
35. G. J. Schulz and R. E. Fox, Phys. Rev. **106**, 1179 (1957).
36. A. K. Bhatia and A. Temkin, Phys. Rev. A **23**, 3361 (1981).

37. K. T. Chung and B. F. Davis, "Hole-Projection Method for Calculating Feshbach Resonances and Inner-Shell Vacancies," *Autoionization: Recent Developments and Applications*, ed. by A. Temkin, 1985, pp. 73-102.
38. B. R. Junker, *J. Phys. B* **15**, 4495 (1982).
39. J. N. H. Brunt, G. C. King, and F. H. Read, *J. Phys. B* **10**, 433 (1977).
40. A. Temkin, A. K. Bhatia, and Y. S. Kim, *J. Phys. B.* **19**, L701, 1986).
41. A. K. Bhatia and A. Temkin, *Phys. Rev. A* **37**, 1415 (1988).
42. A. Temkin and R. J. Drachman, *J. Phys. B Lett.* **33**, L505 (2000).
43. D. Vrinceanu, A. Z. Msezane, D. Bessis, and A. Temkin, *Phys. Rev. Lett.* **85**, 3256 (2001).
44. A. Temkin and K. V. Vasavada, *Phys. Rev.* **160**, 109 (1967).
45. E. S. Chang and A. Temkin, *Phys. Rev. Lett.* **23**, 399 (1969).
46. D. M. Chase, *Phys. Rev.* **104**, 838 (1969).
47. A. Temkin and F. H. M. Faisal, *Phys. Rev. A* **3**, 520 (1971).
48. D. E. Golden, N. F. Lane, A. Temkin, and E. Gerjouy, *Rev. Mod. Phys.* **43**, 642 (1971).
49. N. Chandra and A. Temkin, *Phys. Rev. A* **13**, 188 (1976).
50. R. J. Drachman, *Phys. Rev.* **138**, A1582 (1965).
51. A. Dalgarno and N. Lynn, *Proc. Phys. Soc. (London)* **A70**, 223 (1957).
52. B. H. Bransden, *Proc. Roy. Soc. (London)*, **A79**, 190 (1962).
53. S. K. Houston and R. J. Drachman, *Phys. Rev. A* **3**, 1335 (1971).
54. F. E. Harris, *Phys. Rev. Letters* **19**, 173 (1967).
55. A. K. Bhatia, A. Temkin, R. J. Drachman, and H. Eiserike, *Phys. Rev. A* **3**, 1328 (1971).
56. A. K. Bhatia, A. Temkin, and H. Eiserike, *Phys. Rev. A* **9**, 219 (1974).
57. E. L. Chupp, D. J. Forrest, P. R. Higbie, A. N. Suri, and C. Tsai, *Nature*, **241**, 333 (1973).
58. M. Leventhal, C. J. MacCallum, A. F. Hutters, and P.D. Stang, *Ap. J.* **240**, 338 (1978).
59. R. A. Ferrell, *Rev. Mod. Phys.* **28**, 308 (1956).
60. A. K. Bhatia, R. J. Drachman, and A. Temkin, *Phys. Rev. A* **9**, 223 (1974).
61. A. K. Bhatia, R. J. Drachman, and A. Temkin, *Phys. Rev. A* **16**, 1719 (1977).
62. J. W. Humberston and J. B. G. Wallace, *J. Phys. B* **5**, 1172 (1972).
63. J. W. Humberston (unpublished).
64. S. K. Houston and R. J. Drachman (unpublished).
65. R. J. Drachman, *Phys. Rev.* **173**, 190 (1968).

66. A. P. Mills, Jr., Phys. Rev. Lett. **46**, 717 (1981).
67. A. P. Mills, Jr., Phys. Rev. Lett. **50**, 671 (1983).
68. A. K. Bhatia and R. J. Drachman, Phys. Rev. **28**, 2523 (1983).
69. A. Ore and J. L. Powell, Phys. Rev. **75**, 1696 (1949).
70. I. Harris and L. M. Brown, Phys. Rev. **105**, 1656 (1957).
71. A. P. Mills, Jr., Phys. Rev. A **24**, 3242 (1981).
72. A. K. Bhatia, Phys. Rev. A **2**, 1667 (1970); G. W. Drake, Phys. Rev. Lett., **24**, 126 (1970).
73. M. Rotenberg and J. Stein, Phys. Rev. **182**, 1 (1969).
74. A. K. Bhatia and R. J. Drachman, Phys. Rev. A **32**, 3745 (1985).
75. S. Chandrasekhar, Astrophys. J. **102**, 223 (1945); S. Chandrasekhar and D. D. Elbert, *ibid* **128**, 633 (1958).
76. H. A. Bethe and R. Peierls, Proc. R. Soc. London, Ser. A **148**, 146 (1935).
77. T. Ohmura and H. Ohmura, Phys. Rev. **118**, 154 (1960).
78. K. L. Bell and A. E. Kingston, Proc. Phys. Soc. (London) **90**, 895 (1967).
79. S. J. Ward, J. W. Humberston, and M. R. C. McDowell, J. Phys. B **18**, L525 (1985).
80. A. K. Bhatia and R. J. Drachman, Phys. Rev. A **30**, 2138 (1984).
81. A. K. Bhatia, R. J. Drachman, and L. Chatterjee, Phys. Rev. A **38**, 494 (1988).
82. A. K. Bhatia and R. J. Drachman, Comments At. Mol. Phys. **22**, 281 (1989).
83. A. K. Bhatia and R. J. Drachman, Phys. Rev. A **45**, 7752 (1992).
84. A. K. Bhatia and R. J. Drachman, J. Phys. B **27**, 1299 (1994).
85. W. G. Sturrs, E. A. Hassels, P. W. Arcunni, and S. R. Lundeen, Phys. Rev. A **38**, 135 (1988); Z. W. Fu, E. A. Hassels, S. R. Lundeen, *ibid.* **46**, R5313 (1992).
86. P. L. Jacobson, D. S. Fisher, C. W. Fehrenbach, W. G. Sturrs, and S. T. Lundeen, Phys. Rev. A **56**, R4361 (1997); **57**, 4065(E) (1998).
87. D. M. Bishop and B. Lam, Mol. Phys. **65**, 679 (1988); J. F. Babb, *ibid.* **81**, 17 (1994).
88. A. K. Bhatia and R. J. Drachman, Phys. Rev. A **59**, 205 (1999).
89. B. Gre'maud, D. Delande, and N. Billy, J. Phys. B **31** 383 (1998); R. E. Moss, Chem. Phys. Lett. **172**, 458 (1990); A. K. Bhatia, Phys. Rev. A **58**, 2787 (1998).
90. J. Shertzer and C.H. Greene, Phys. Rev. A **58**, 1082 (1998).
91. A. K. Bhatia and R. J. Drachman, Phys. Rev. A **61**, 035203 (2000).
92. R. E. Moss, J. Phys. B **32**, L89 (1998).

93. A. K. Bhatia and R. J. Drachman, *Phys. Rev. A* **58**, 4470 (1998).
94. P. J. Leonard, *At. Data Nucl. Data Tables* **14**, 22 (1974).
95. A. K. Bhatia and R. J. Drachman, *Phys. Rev. A* **57**, 4301 (1998).
96. A. Dalgarno and A. L. Stewart, *Proce. Phys. Soc. London* **76**, 49 (1960).
97. S. P. Goldman and G. W. F. Drake, *J. Phys. B* **16**, L183 (1983); **17**, L197 (1984).
98. S. E. Haywood and J. D. Morgan III, *Phys. Rev. A* **32**, 3179 (1985).
99. R. W. F. Drake, in *Long-Range Casimir Forces: Theory and Recent Experiments*, edited by F. S. Levin and D. A. Micha (Plenum, New York, 1993), p. 107.
100. R. J. Drachman, in *Long-Range Casimir Forces: Theory and Recent Experiments*, edited by F. S. Levin and D. A. Micha (Plenum, New York, 1993), p. 219 and reference therein.
101. R. J. Drachman and A. K. Bhatia, *Phys. Rev. A* **51**, 2926 (1995).
102. H. A. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1957), p 192.
103. N. E. Rothery, C. H. Storry, and E. A. Hassels, *Phys. Rev. A* **51**, 2919 (1995).
104. A. K. Bhatia and R. J. Drachman, *Phys. Rev. A* **55**, 1842 (1997).
105. E. J. Kelsey and L. Spruch, *Phys. Rev. A* **18**, 15 (1978); **18**, 1055 (1978) | J. Bernabeu and R. Tarrach, *Ann. Phys. (N.Y.)* **102m** 323 (1976).
106. C. K. Au, G. Feinberg, and J. Sucher, *Phys. Rev. Lett.* **53**, 1145 (1984).
107. S. P. Goldman and G. W. F. Drake, *Phys. Rev. Lett.* **68**, 1683 (1992).
108. A. K. Bhatia and R. J. Drachman, *Phys. rev. A* **60**, 2848 (1999).
109. R. J. Drachman and S. K. Houston, *Phys. Rev. A* **12**, 885 (1975).
110. S. K. Houston and R. J. Drachman, *Phys. Rev. A* **7**, 819 (1973).
111. Y. K. Ho, *Phys. Rev. A* **17**, 1675 (1978).
112. J. DiRienzi and R. J. Drachman, *Phys. Rev. A* **65**, 032721 (2002).
113. J. DiRienzi and R. J. Drachman, *Phys. Rev. A* **66**, 054702 (2002).
114. K. -N. Huang and V. W. Hughes, *Phys. Rev. A* **20**, 706 (1979); **21**, 1071 (1980).
115. R. J. Drachman, *Phys. Rev. A* **22**, 1755 (1980).
116. A. Dalgarno and J. T. Lewis, *Proc. R. Soc. London Ser. A* **233** 70 (1955).
117. S. D. Lakdawala and P. J. Mohr, *Phys. Rev. A* **22**, 1752 (1980).