Journal of Atomic, Molecular, Condensed Matter and Nano Physics
Vol. 12, No. 1, pp. 9–26, 2025
ISSN 2582-8215
Published by RGN Publications

www.rgnpublications.com

DOI: 10.26713/jamcnp.v12i1.3018

Research Article

Variational Principles and Their Applications

A. K. Bhatia

Heliophysics Division, NASA/Goddard Space Flight Center, Greenbelt, MD 20701, USA
anand.k.bhatia@nasa.gov

Received: January 30, 2025 **Accepted:** March 15, 2025 **Published:** October 25, 2025

Abstract. There are many variational calculations of energies of various systems which have applications in Rydberg states and polarizabilities of these systems. There are variational calculations of scattering functions which have applications in calculations of excitation, photoabsorption, and radiative attachment cross sections. A few of these applications are mentioned.

Keywords. Variational principles, Variational calculations, Ritz variational method, Rydberg states, Photoionization, Electron-hydrogen scattering, Positron-hydrogen scattering

PACS. 31.15.xt, 11.80.Fv

1. Introduction and Variational Calculations

The Ritz variational principle has been used to calculate energies of various systems. The simplest calculation is of the helium atom. If the wave function is given by

$$\psi(\vec{r}_1,\vec{r}_2) = Ne^{-\alpha(r_1+r_2)}Y_{00}(\Omega_1)Y(\Omega_2). \tag{1.1}$$

The nonlinear parameter is α, which can be varied to obtain the lowest energy value, and N is the normalization constant. The energy value is given by

$$E = \frac{\langle \psi H \psi \rangle}{\langle \psi \psi \rangle}. \tag{1.2}$$

Assuming that the nucleus is of infinite mass, the Hamiltonian H is

$$H = -\nabla_1^2 - \nabla_2^2 - \frac{2Z}{r_1} - \frac{2Z}{r_2} + \frac{2}{r_{12}}. \tag{1.3}$$

The nuclear charge is Z. We find

$$E = 2\alpha^2 - 4Z\alpha + \frac{5\alpha}{4}, \tag{1.4}$$

$\frac{dE}{d\alpha} = 0$ gives $\alpha = \frac{27}{16}$. Substituting this value in eq. (1.4), we find $E = -2(27/16)^2 = -5.695$ Ry, the calculated ionization energy. This approximation is called a close-shell approximation. This value is far below the energy required to remove both electrons, which is approximately 5.807 Ry (Pekeris [37]). We use Ry units, unless stated otherwise. It was suggested by Hylleraas [30] that the interelectron distance $r_{12} = |\vec{r}_1 - \vec{r}_2|$, where r_1 and r_2 are the distances of the two electrons from the nucleus should be included in the wave function. Therefore, in a variational calculation, we should use a wave function of the form

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{lmn} C_{lmn} r_1^l r_2^m r_{12}^n e^{-\gamma r_1 - \delta r_2} \pm (1 \leftrightarrow 2). \tag{1.5}$$

This is known as a Hylleraas-type wave function. The plus sign refers to the singlet states and the minus sign refers to the triplet states. Optimizing the nonlinear parameters to get the lowest energy, we get for $\gamma = 3.22$, $\delta = 2.17$, and $N = 220$ terms in the wave function $E = -5.8074487$ Ry for the ground state of He (Bhatia [2]). Drake [26, 27] has obtained very accurate results for the ground state as well as for the excited states by choosing a wave function with four nonlinear parameters. Let

$$\psi(\vec{r}_1, \vec{r}_2, \gamma_i, \delta_i) = \sum_{lmn} C_{lmn} r_1^l r_2^m r_{12}^m e^{-\gamma_i r_1 - \delta_i r_2} \pm (1 \leftrightarrow 2). \tag{1.6}$$

The final trial function chosen is of the form

$$\psi(\vec{r}_1, \vec{r}_2) = \psi(\vec{r}_1, \vec{r}_2, \gamma_1, \delta_1) + \psi(\vec{r}_1, \vec{r}_2, \gamma_2, \delta_2). \tag{1.7}$$

Some of Drake's results are given in Tables 1 and 2.

Table 1. Variational energies S states of He (a.u.)

Number of terms	1^1S	Number of terms	2^3S
464	−2.903724377033946	451	−2.17522937823678730
561	−2.903724377034076	539	−2.17522937823678998
674	−2.903724377034107	640	−2.17522937823679080
797	−2.903724377034116	747	−2.17522937823679111
extrapolated	−2.903724377034119	extrapolated	−2.17522937823679123
	2^1S		
451	−2.145974046053418		
539	−2.145974046054065		
640	−2.14597046054304		
747	−2.145974046054378		
extrapolated	−2.145974046054426		

Table 2. Variational energies of P states He (a.u.)

Number of terms	2^1P	2^3P
436	−2.123843086497525	−2.133164190777932
539	−2.123843086497975	−2.133164190778968
658	−2.123843086498068	−2.133164190779216
724	−2.123843086498084	−2133164190779250
804	−2.123843086498091	−2.133164190779268
extrapolated	−2.123843086498094	−2.133164190779279

2. Asymptotic Method

Drake [26, 27] has calculated energy values of high-lying states, called Rydberg states. A disadvantage of this method is that optimization of nonlinear parameters has to be carried out for each state. This method involves lot of computer time and is very tedious. Drachman [24, 25] indicated that the outer electron polarizes the core. Considering He atom, the core consists of He^+. If the outer electron is at a distance x from the nucleus, then polarization potential in terms of dipole, quadrupole and other polarizabilities is given by

$$U(x) = -\frac{\alpha_1}{x^4} - \frac{\alpha_2}{x^6} + \frac{\delta}{x^7} - \frac{\alpha_3}{x^8} - \frac{\varepsilon}{x^9}. \tag{2.1}$$

In addition to these polarizabilities, there are non-adiabatic polarizabilities contributing to the potential seen by the outer electron

$$U'(x) = \frac{6\beta_1}{x^6} + \frac{15\beta_2}{x^8}. \tag{2.2}$$

Various values [25] are

$$\alpha_1 = \frac{9}{32},\ \alpha_2 = \frac{15}{64},\ \alpha_3 = \frac{524}{1024},\ \beta_1 = \frac{42}{512},\ \beta_2 = \frac{107}{2048},\ \gamma = \frac{519}{12288}, \text{ and } \varepsilon = \frac{4229}{32768}.$$

Drachman has called this method an asymptotic method. The polarizabilities of the core can be calculated and then the expectation values of $1/x^n$ can be calculated for any hydrogenic NL state ([26, 27] [21]). Below, in Table 3, we compare the energies of some of the Rydberg states obtained by the variational method of Drake and the asymptotic method of Drachman. The results in Table 3 are given in MHz, where 1 Ry= 3.289×10^9 MHz.

Comparison of various energy values of $N = 10$ with experimental values (Hassels *et al*. [29]) are given in Table 4. The theoretical values include relativistic corrections.

The asymptotic method has been used for Rydberg states in lithium also. The generalized polarizabilities have been calculated by Bhatia and Drachman [9]. In the calculation of the Rydberg states, Bhatia and Drachman included relativistic corrections, retardation, radiative, and Lamb shift corrections. These are given in Table 5 along with the uncorrected shifts (Drachman and Bhatia [22]).

In Table 6 we compare level differences, in MHz, for lithium between theory and experiment (Rothery *et al*. [38]). The earlier results given by Drachman and Bhatia [22] do not include corrections given in Table 5. We find that the agreement with the experiment is very good, showing that the asymptotic approach gives accurate results for the energy levels, and importance of corrections is given in Table 5.

Table 3. Comparison of the asymptotic nonrelativistic energy shifts in MHz with the accurate results of Drake [26, 27]

N	L	Asymptotic	Variational	V-A
5	4	$-4677,0562 \pm 1.011$	-4676.9348501	0.1213
10		-741.8875 ± 0.521	-741.8935917	-0.0061
6	5	-959.6277 ± 0.0022	959.61668162	0.0119
10		-257.9853 ± 0.0059	-257.9830286	0.0023
7	8	-256.39849 ± 0.00010	-256.3984126065	0.00008
10		-105.82980 ± 0.00014	-105.829683489	0.00012
9	8	$-30.71230412 \pm 2 \times 10^{-7}$	N/A	
10		$-24.17863264 \pm 4 \times 10^{-7}$	N/A	

Table 4. Comparison of theoretical energy values [MHZ] with experiment

$L \to L'$	Theory	Experiment	Experiment-Theory
$4 \to 5$	$490.9566 \pm .521$	$491.0052 \pm .0005$	$0.0486 \pm .521$
$5 \to 6$	$157.0499 \pm .0059$	$157.0524 \pm .0002$	$0.0025 \pm .0059$
$6 \to 7$	$60.81480 \pm .00014$	$60.8159 \pm .00002$	$0.0011 \pm .0002$
$7 \to 8$	27.17502	$27.1747 \pm .0005$	$-0.0003 \pm .0005$

Table 5. Effect of small corrections on the uncorrected intervals, in MHz, for the $N = 10$ manifold of Li

L	Uncorrected shift	Relativistic polarizability	Retardation	Lamb shift	Total
4	-535.343	0.1201	0.0654	-0.0251	-535.183
5	-195.5397	0.0416	0.0212	-0.0087	-195.4856
6	-86.2932	0.0170	0.0079	-0.0036	-86.2719
7	-43.49739	0.0078	0.0033	-0.0016	-43.4879
8	-24.02231	0.0039	0.0014	-0.0008	-24.0178
9	-14.013679	0.0020	0.0006	-0.0004	-14.0115

Table 6. Comparison of level differences for lithium, in MHz, between theory and experiment

Interval	Experiment [38] – Theory [22]	Experiment [38] – Theory[a]	Standard deviation
10G-10H	-0.08	0.02	0.11
10H-10I	-0.0326	0.0003	0.0048

[a] Theory includes all the corrections given in Table 5.

Similar calculations have been carried out for C IV, O VI, and Ne VIII [6]. In Table 7, we give some results from [6].

Table 7. Theoretical fine-structure intervals in MHZ

	C IV	O VI	Ne VIII
Interval	Transition	Transition	Transition
10F-10G	$(21.54 \pm 0.71) \times 10^3$	$(42.8 \pm 1.3) \times 10^3$	$(8.09 \pm 0.18) \times 10^4$
12G-12H	3438 ± 23	8840 ± 6.8	21241 ± 85
12H-12I	1466.9 ± 1.1	4779.46 ± 0.43	12988.2 ± 4.4

3. H_2 and D_2 Molecular Ions

Experiments [28, 42] to determine polarizabilities of H_2^+ and D_2^+ prompted us to calculate wave functions to infer polarizabilities. Reversing electron and proton masses did not give any satisfactory results, no matter what the number of terms was. This wave function does not allow protons to remain in their positions and treats them like electrons. We did not want to use the Born approximation to calculate the motion of protons, rather we wanted to treat the system as a three-body system. To overcome this difficulty, Richard Drachman suggested that the power n of r_{12}, which represent interproton distance should be very high and the corresponding nonlinear parameter should be half of n,

$$\psi(\vec{r}_1,\vec{r}_2) = \sum_{lmn} C_{lmn} r_1^l r_2^m r_{12}^n e^{-\gamma r_1 - \delta r_2 - b r_{12}} \pm (1 \leftrightarrow 2). \tag{3.1}$$

The Hamiltonian for these systems is

$$H = -\nabla_1^2 - \nabla_2^2 - 2\mu \vec{\nabla}_1 \cdot \vec{\nabla}_2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{2}{r_{12}}. \tag{3.2}$$

The 3rd term is the mass polarization term, $\mu = \frac{M}{M+1}$, where M is the mass of a proton when the electron mass is taken as 1. This wave function helped a lot. With $n = 10$, we [18] obtained for 615 terms $E = -1.194277909$ Ry for H_2^+, compared to -1.194278126 Ry obtained by Frolov and -1.197572175 Ry for D_2^+ compared to -1.197577413 Ry obtained by Bishop and Chung [20]. We [18] also calculated expectation values of various parameters for H_2^+ and D_2^+. We [8] calculated the dipole polarizabilities for H_2^+ and D_2^+, using the expression given below

$$\alpha_1 = \frac{4}{\mu^2(1+\mu)^2} \sum_p \frac{|\langle 0|z_A + z_B|p\rangle|^2}{E_p - E_0} a_0^3. \tag{3.3}$$

The $L = 1$ states are represented by p. In Table 8, we give convergence of the polarizabilities as the number of p states is increased.

In Table 9, we compare our results with the results of other calculations. We find that the present calculations treating the system as a three-body system gives polarizabilities which agree with the experimental results.

Table 8. Convergence of dipole polarizabilities for H_2^+ and D_2^+ with the number of terms, N_p is increased

N_p	$\alpha_1(H_2^+)$	$\alpha_1(D_2^+)$
120	3.149851	3.012308
165	3.159469	3.037802
220	3.164864	3.054261
286	3.167134	3.060808
364	3.167953	3.067089

Table 9. Polarizabilities of H_2^+ and D_2^+

Method	$\alpha_1(H_2^+)$	$\alpha_1(D_2^+)$
Experiment[a]	3.1681(7)	3.0712(7)
Born-Oppenheimer[b]	3.1713	3.0731
Present	3.1680	3.061
Finite-Element[c]	3.1682	3.0714(4)

[a]Ref. [31]; [b]Refs. [1, 19]; [c]Ref. [41]

4. Muon-Catalyzed Fusion

Long ago it was thought that the fusion reaction could be used to generate energy:

$$[t\,d\,\mu] \rightarrow \alpha + \mu + n + 17.58 \text{ MeV kinetic energy.} \tag{4.1}$$

Binding energies of various muonic molecules are required to study the fusion processes. In Table 10, we [5] give binding energies of the rotational state J and vibrational state v of muonic molecules.

Table 10. Binding energies (eV) for various muonic molecules with quantum numbers (Jv)

Molecule	$(Jv) = (00)$	(01)	(10)	(11)
$pp\mu$	253.1523322		107.2659714	
$pd\mu$	221.5494096		97.4981602	
$pt\mu$	213.8401794		99.1265014	
$dd\mu$	325.0735402	35.8443605	226.6816786	1.9748717
$dt\mu$	319.139722259	34.8344912	232.4715935	0.6601721
$tt\mu$	362.9097696	83.7712165	289.1417829	45.2058563

5. Positronium Negative Ion

Since all the particles have the same mass, we [7] using the Hamiltonian given in eq. (3.2) to calculate binding energy of Ps^- ion. We give in Table 11 binding energies for different number of terms in the wave function. We used the binding energy to calculate photodetachment of the positronium negative ion.

Table 11. Binding energy of Ps^- ion

Number of terms	Binding energy (Ry)
120	0.024009966
165	0.024010079
220	0.024010113

6. Hyperfine Structure of the Lithium Ground State

Hyperfine structure depends on the delta function $\delta(r)$. There have been very accurate variational calculations of the energy of the ground state of lithium by Larsson [33], using a 100-term Hylleraas type wave function. Using this type of wave function and delta function, value of the Fermi-contact term has been calculated. Because of the delta function in the matrix element, value of the wave function at $r = 0$ is very important. However, if a global operator (Drachman and Sucher [23, 43]) instead of the delta function is used, even a configuration interaction type wave function can yield accurate results for the Fermi-contact term (Bhatia and Sucher [4]). We define

$$f = 4\pi\left\langle \psi \middle| \sum_i g_z(i) \middle| \psi \right\rangle. \tag{6.1}$$

In the above equation

$$g(i) = \sum_i \delta(r_i). \tag{6.2}$$

We define

$$f' = 4\pi\left\langle \bar{\psi} \middle| \sum_i g'_z | \bar{\psi} \right\rangle. \tag{6.3}$$

We have replaced the exact ψ by an approximate $\bar{\psi}$, and g_z by g'_z, where

$$g'_z = \sum_i D_i,, \tag{6.4}$$

$$D_i = \frac{m}{2\pi}\frac{\partial V}{\partial r_i} - \frac{l_i}{2\pi r_i^2}. \tag{6.5}$$

In the above, $\vec{l}_i = \vec{r}_i \times \vec{p}_i$ and

$$V = \sum_i \left(-\frac{Z}{r_i}\right) + \sum_{i<j} 1/r_{ij}. \tag{6.6}$$

In Table 12, we give a comparison of two ways of calculating the Fermi contact term.

Table 12. Energy values and Fermi contact term against N, the number of terms in the configuration interaction wave function

N	Energy E(au)	f_N	f'_N
3	−7.442225	3.2852	3.1177
6	−7.445404	3.0018	2.8608
10	−7.445413	3.0057	2.8644
16	−7.446614	3.0339	2.8855
20	−7.469530	3.0001	2.8352
24	−7.469904	3.0003	2.8261
34	−7.470761	3.0539	2.8782
40	−7.473393	3.0717	2.9014
100-term Hylleraas wave function[a]	−7.479025	2.906	—
Experiment[b]	−7.478069		2.9062

[a] Larsson [33]; Kusch and Taub [32]

We see that the use of the global identity gives accurate results even for an approximate wave function.

7. Continuum Functions

Continuum or scattering functions are required to calculate elastic scattering, momentum transfer, spin-flip cross sections. In addition to these, they are also required to calculate excitation and photon absorption cross sections. The simplest approximation is a static approximation:

$$\Psi(\vec{r}_1,\vec{r}_2) = u(\vec{r}_1)\phi_0(\vec{r}_2). \tag{7.1}$$

In eq. (7.1), $\vec{r}_1$ and $\vec{r}_2$ are the distances of the incident and bound electrons from the nucleus, $u(\vec{r}_1)$ is the scattering function and $\phi_0(\vec{r}_2)$ is the target function. Exchange between the identical particle is important. Therefore, eq. (7.1) must be modified accordingly:

$$\Psi(\vec{r}_1,\vec{r}_2) = u(\vec{r}_1)\phi_0(\vec{r}_2) \pm (1 \leftrightarrow 2). \tag{7.2}$$

The plus sign refers to the singlet states and the minus sign refers to the triplet states. In eqs.(7.1), (7.2),

$$u(\vec{r}_i) = \frac{u(r_i)}{r_i} Y_{L0}(\Omega_1), \tag{7.3}$$

where Ω_1 is the solid angle, measured in radians and expressed in terms of spherical polar angles θ_1 and φ_1. The ground state function is given by

$$\phi_0(\vec{r}_2) = 2e^{-r_2} Y_{00}(\Omega_2). \tag{7.4}$$

The scattering function u is of the incident particle is obtained from

$$\int Y_{L0}(\Omega_1)\phi_0(\vec{r}_2)|H-E|\Psi d\Omega_1 d\vec{r}_2 = 0. \tag{7.5}$$

Morse and Allis [34] carried out the exchange approximation calculations in 1933. Assuming that the nucleus is of infinite mass and remains fixed so that the recoil of the nucleus can be neglected, the Hamiltonian H from eq. (1.3) and energy E (H and E in Rydberg units) are given by

$$H = -\nabla_1^2 - \nabla_2^2 - \frac{2Z}{r_1} - \frac{2Z}{r_2} + \frac{2}{r_{12}}, \tag{7.6}$$

$$E = -Z^2 + k^2. \tag{7.7}$$

Z is the nuclear charge and k is the momentum of the incident electron. Using eq. (7.5), we get the equation for the scattering function

$$\left[\frac{d^2}{dr^2} - \frac{L(L+1)}{r^2} + V_d(r) + k^2\right] u(r) \pm 4Z^2 \left[(Z^2+k^2)V_L(r)\delta_{L0} - \frac{2}{2L+1} y_L(r)\right] = 0, \tag{7.8}$$

$$V_d(r) = \frac{2(Z-1)}{r} + 2e^{-Zr}\left(1+\frac{1}{r}\right), \tag{7.9}$$

$$y_L(r) = \frac{1}{r^L}\int_0^r x^{L+1}\phi_0(x)u_L(x)dx + r^{L+1}\int_r^\infty \phi_0(x)\frac{u_L(x)}{x^L}dx. \tag{7.10}$$

We obtain the static approximation by neglecting the exchange terms. The scattering function behaves asymptotically like $\sin\left(kr - \frac{L\pi}{2} + \eta_L\right)$, where η_L is the phase shift for the incident angular momentum L. Elastic scattering cross sections are determined as a function of phase shifts

$$\sigma_L(\pi a_0^2) = (2L+1)[3\sin^2(\eta_-) + \sin(\eta_+)]/k^2. \tag{7.11}$$

The triplet phase shifts are indicated by $\eta_+$and singlet phase shifts are indicated by η_-.

In the presence of the incident electron, the target is perturbed. Temkin [45] has shown that using the adiabatic approximation in the first-order perturbation theory and the dipole part of the resulting perturbed wave function that in the presence of the incident electron r_1 the effective wave function of the target can be written as

$$\Phi^{pol}(\vec{r}_1,\vec{r}_2) = \phi_0(\vec{r}_2) - \frac{\varepsilon(r_1,r_2)}{r_1^2}\frac{u_{1s\to p}(r_2)}{r_2}\frac{\cos(\theta_{12})}{\sqrt{Z\pi}}. \tag{7.12}$$

The functions $u_{1s\to p}$ are given by

$$u_{1s\to p}(r_2) = e^{-Zr_2}\left(\frac{Z}{2}r_2^3 + r_2^2\right). \tag{7.13}$$

The angle θ_{12} is the angle between r_1 and r_2. Temkin and Lamkin [44] introduced the step function

$$\varepsilon(r_1,r_2) = \begin{cases} 1, & r_1 > r_2, \\ 0, & r_1 < r_2. \end{cases} \tag{7.14}$$

The step function ensures that the polarization takes place only when the incident electron is outside the target electron. The scattering function is obtained from eq. (7.5) by replacing $\phi_0(\vec{r}_2)$ in eq. (7.2) by Φ^{pol} given in eq. (7.12).

This is called the method of polarized orbitals (PO). This method has been used extensively over the years. However, the method is not variationally correct, i.e., the phase shifts obtained have no bounds. We would like to improve the method so that not only long-range correlations are included but short-range correlations are also included. We would like the method to be variationally correct. Furthermore, we want the polarization function in eq. (7.12) to be valid at all distances r_1. We, therefore, replace the step function $\varepsilon(r_1,r_2)$ by a cutoff of the form

$$\chi_\beta(r_1) = (1 - e^{-\beta r_1})^n. \tag{7.15}$$

The exponent $n \geq 3$. This function gives us another nonlinear parameter β, which depends on k, to optimize the results. Another form of a smooth cutoff is given by Shertzer and Temkin [40],

$$\chi_{ST} = 1 - e^{-2Zr_1}\left[\frac{(Zr_1)^4}{3} + \frac{4(Zr_1)^3}{3} + 2(Zr_1)^2 + 2Zr_1 + 1\right]. \tag{7.16}$$

These forms ensure that $\chi(r_1)/r_1^2 \to 0$ when $r_1 \to 0$. The polarized wave function is given by

$$\Phi^{pol}(\vec{r}_1,\vec{r}_2) = \phi_0(\vec{r}_2) - \frac{\chi(r_1)}{r_1^2}\frac{u_{1s\to p}(r_2)}{r_2}\frac{\cos(\theta_{12})}{\sqrt{Z\pi}}. \tag{7.17}$$

In eq. (7.17), the cutoff function can be of the form given in eq. (7.15) or eq. (7.16). Short-range correlations are included by augmenting the function in eq. (7.2) as

$$\Psi(\vec{r}_1,\vec{r}_2) = u(\vec{r}_1)\Phi^{pol}(\vec{r},_1\vec{r}_2) \pm (1 \leftrightarrow 2) + \sum C_i \Phi_L^i(\vec{r}_i,\vec{r}_2). \tag{7.18}$$

The correlation functionΦabove for any angular momentum L are of the Hylleraas type. They can be written using the Euler angle decomposition [35]. The equation for the scattering is obtained from

$$\int d\Omega_1 d\vec{r}_2 Y_{L0}\Phi^{pol}(\vec{r}_1,\vec{r}_2)|H - E|\Psi(\vec{r}_1,\vec{r}_2) = 0. \tag{7.19}$$

The resulting equation for the scattering function is very complicated. It is given in [14]. We call the present formalism a hybrid theory. In Table 13, we compare the phase shifts obtained for the scattering of an electron from a hydrogen atom using the method of polarized orbitals and the hybrid theory.

Table 13. Singlet and triplet phase shifts η (radians) for e-H scattering

Incident k	PO	Hybrid theory	PO	Hybrid theory
	Singlet phase shifts		Triplet phase shifts	
[a]0	5.8	6.00092	1.9	1.900
0.1	2.553	2.55372	2.949	2.93856
0.2	2.144	2.06699	2.732	2.71751
0.3	1.750	1.69853	2.519	2.49987
0.4	1.469	1.41561	2.320	2.29465
0.5	1.251	1.20112	2.133	2.10544
0.6		1.04110		1.93322
0.7	0.930	0.93094	1.815	1.77998
0.8	0.853	0.88768	1.682	1.64425

[a] $k = 0$ results represent the scattering lengths

The scattering length a given in the above table is defined as

$$\lim_{k\to 0} k\cot\eta = -1/a. \tag{7.20}$$

We see that phase shifts obtained by two methods are close, except that the phase shifts obtained using the hybrid theory are lower than the exact phase shifts, that is they have lower bounds to the exact phase shifts. There are other methods like the Kohn variational principle, the exterior complex scaling method, close-coupling approximation, and R-matrix formalism. The last method has been extensively used in atomic as well as in molecular physics. In this approach a radius a is defined such that all complications are considered within this radius and simple approximations for functions are used outside this radius. This simplifies the calculations providing accurate results. We cannot discuss all these methods in one article.

Hybrid theory has been used for scattering of positrons, annihilation cross sections, and positronium formation. In Table 10, we give phase shifts for scattering of positrons from hydrogen atoms. These phase shifts, including the contribution from the long-range and short-range correlations, are lower than the exact phase shifts.

Table 14. Positron-hydrogen scattering phase shifts(radians)

K	S-wave	P-wave
0.1	0.14918	0.008871
0.2	0.18803	0.032778
0.3	0.16831	0.06964
0.4	0.12083	0.10047
0.5	0.06278	0.13064
0.6	0.00903	0.15458
0.7	−0.04253	0.17806

Resonance parameters of He and Li^+ have been obtained by calculating phase shifts in the resonance region [10] and fitting these phase shifts to the Breit-Wigner form to obtain the

resonance parameters for any resonance,

$$\eta_{\rm cal}(E) = \eta_0 + AE + \tan^{-1}\frac{0.5\Gamma}{(E_R - E)}, \tag{7.21}$$

$E = k^2$ is the incident energy, $\eta_{\rm cal}$ are the calculated phase shifts, η_0, A, Γ, and E_R are the fitting parameters. E_R and Γ represent the resonance position and resonance width. The resonance parameters obtained by this method agree well with those obtained using the Feshbach formalism.

8. Opacity of the Sun's Atmosphere

Opacity of the solar medium is due to Thomson scattering, bound-bound transitions, photodetachment (bound-free) or free-free transitions. In 1939, it was suggested by Wildt [47] that the important source of opacity in the solar atmosphere could be due the photodetachment (bf) of negative hydrogen ions:

$$h\nu + H^- \rightarrow e + H. \tag{8.1}$$

There are also free-free transitions which account for the continuous spectrum of the Sun

$$h\nu + e^- + H \rightarrow e^- + H. \tag{8.2}$$

In eq. (8.1) H^- can be replaced by Ps^-, and free-free transitions due to electrons in eq. (8.2) can also be due to positrons. We also consider photodetachment of the negative positronium ions and free-free transitions due to positrons. The contribution due to the photodetachment of Ps^- and free-free transitions due to positrons to the opacity of the Sun and stellar medium have not been considered earlier. In Table 15, we give some results for comparison. The cross sections have been Maxwellian averaged at a temperature of 6300 K.

Table 15. Comparison of bound-free (bf) and free-free cross sections ($\rm cm^2$) for electrons and positrons at $T = 6300$ K

	Electrons			Positrons		
λ(Å)	$\sigma(bf)$	σ_{ff}	$\sigma(bf)+\sigma_{ff}$	$\sigma(bf)$	σ_{ff}	$\sigma(bf)+\sigma_{ff}$
3505	2.29(−17)	4.28(−20)	2.29(−17)	9.95(−18)	4.14(−21)	9.95(−18)
7594	4.10(−17)	1.88(−19)	4.17(−17)	3.17(−17)	1.56(−20)	3.17(−17)
9113	4.13(−17)	2.69(−19)	4.16(−17)	4.17(−17)	2.15(−20)	4.17(−17)
15188	7.05(−18)	7.45(−19)	7.80(−18)	8.96(−17)	5.38(−20)	8.97(−17)
22783	0.00	1.68(−18)	1.68(−18)	1.65(−16)	1.13(−19)	1.65(−16)
30377	0.00	2.99(−18)	2.99(−18)	2.53(−16)	1.96(−19)	2.53(−16)
44565	0.00	6.74(−18)	6.74(−18)	4.64(−16)	4.30(−19)	4.64(−16)
91130	0.00	2.70(−15)	2.70(−15)	1.30(−15)	1.68(−18)	1.30(−15)

9. Photoionization

The derivation of the photoabsorption cross section is given in [15]. In the length form and in the dipole approximation for the process in eq. (8.2), it is given by

$$\sigma(a_0^2) = 4\pi\alpha k(I + k^2)|\langle\Psi_f|z_1 + z_2|\Phi\rangle|^2. \tag{9.1}$$

In the above equation, $\alpha = 1/137.036$ is the fine-structure constant, I is the ionization potential, $z_i = r_i\cos(\theta_i)$ are the dipole transition operators, and k is the momentum of the outgoing

electron. The function Φ represents the bound state wave function of the system being photodetached or photoionized, and Ψ is the wave function of the outgoing electron and the remaining atom or ion. In Table 16, we [13] give cross sections of the photodetachment of H^-, without the short-range correlations. In Figure 1, we indicate these cross sections, as well as those obtained including the short-range correlations. We see that the short-range correlations have some effect on the cross sections. We also give in the figure results obtained using the Ohmura and Ohmura approach [36].

Table 16. Photodetachment cross sections[a] in (Mb) of H^-

K	Cross section	k	Cross section
0.01	0.0245	0.26	38.3850
0.02	0.1959	0.3	34.9684
0.03	0.6444	0.4	24.2537
0.04	1.4736	0.5	15.8692
0.05	2.7480	0.6	10.4924
0.06	4.4914	0.7	7.1258
0.07	6.6844	0.74	6.1530
0.1	15.2365	0.8	4.9768
0.2	38.3688	0.8544	4.1421
0.23	39.4354	0.8631	4.0224
0.24	39.2882	0.8660	3.9846
0.25	38.9121		

[a] Cross sections without correlations

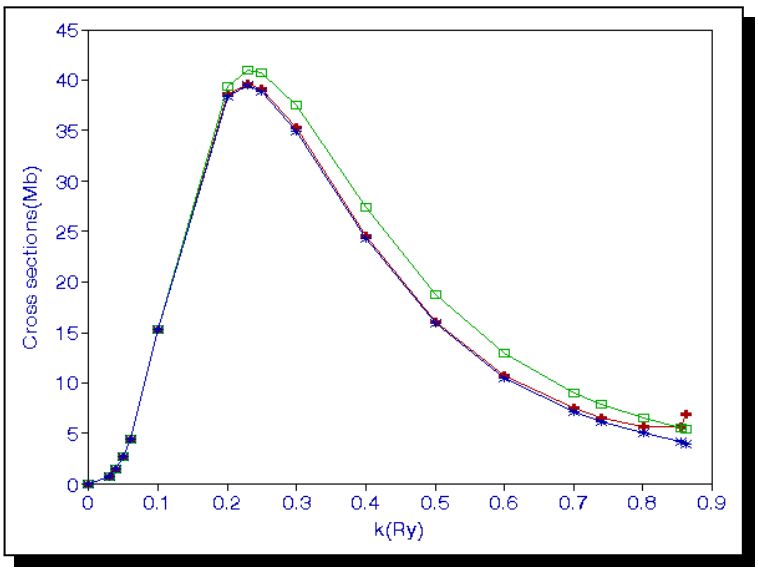

Figure 1. Photodetachment of negative hydrogen ion. The lowest curve is without the short-range cross sections given in Table 16. The middle curve includes short-range correlations. The top curve represents the cross sections are obtained by Ohmura and Ohmura [36] using the effective range theory

Table 17. Photoionization cross sections (Mb) for the ground state of He obtained with correlations and a comparison with the results of the R-matrix and experiments

K	Hybrid theory [13]	R-matrix [35]	Experiment [46]	Experiment [39]
0.1	7.3300	7.295	7.51	7.44
0.2	7.1544	7.115	7.28	7.13
0.3	6.8716	6.838	6.93	6.83
0.4	6.4951	6.474	6.49	6.46
0.5	6.0461	6.006	5.99	6.02
0.6	5.5925	5.535	5.46	5.55
0.7	5.0120	4.995	4.92	5.04
0.8	4.4740	4.482	4.38	4.51
0.9	3.9649			
1.0	3.4654	3.476	3.38	3.48
1.1	3.0206	3.023	2.91	3.00
1.3	2.2561	2.271	2.17	2.19
1.4	1.9821	1.943	1.87	1.89
1.5	1.6817			
1.6	1.6329			

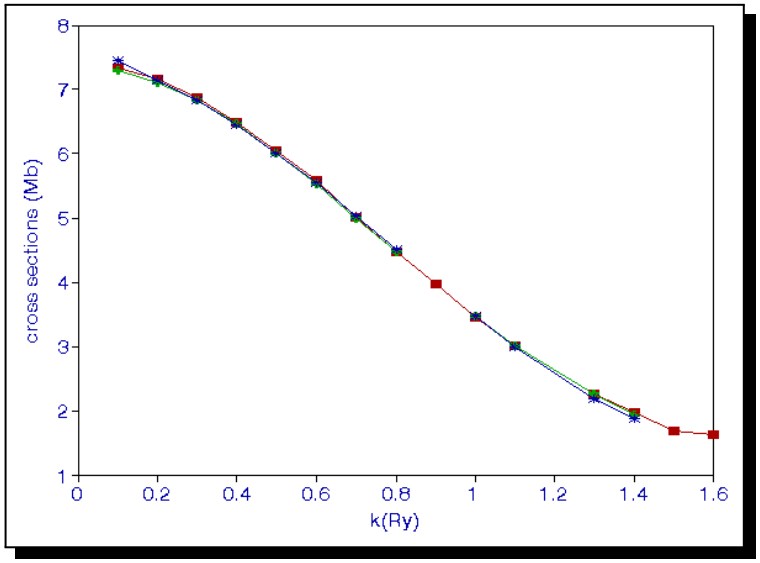

Figure 2. Photoionization of He. A comparison of cross sections calculated using the hybrid theory [13] and R-matrix approximation [35] with the experimental results [39, 46]

Photoionization cross sections of He atom have also been calculated using the hybrid theory [13]. These results along with those using the R-matrix formalism [35] and experimental results [39, 46] are given in Table 17. Figure 2 shows a comparison of these results. These results agree with each other, and it is not possible to distinguish various curves. It shows that the present formulation of the hybrid theory gives accurate results. Similar calculations

have been carried out for Li^+ and for excited states of He and Li^+. Cross sections for radiative attachments have also been calculated. Radiative attachment is given by

$$e^- + H \rightarrow h\nu + H^- . \tag{9.2}$$

10. Excitation

Excitation of S-states by electron and positron impact of atomic hydrogen have been calculated using the hybrid theory for the initial state and plane wave for the final state. The cross section is given by

$$\sigma = \frac{k_f}{k_i} \int |T_{fi}|^2 d\Omega . \tag{10.1}$$

Here k_i and k_f are the initial and final momenta and T_{fi} is a matrix element given by

$$T_{fi} = -(1/4\pi)\langle \psi_f | V | \Psi_i \rangle . \tag{10.2}$$

In the above expression,

$$V = -\frac{2z}{r_1} + \frac{2}{r_{12}} . \tag{10.3}$$

Excitation cross sections of atomic hydrogen $2S$ state are given in by electron-impact in [12] and by positron-impact in [16]. They are shown in Figure 3. We see that the positron-impact cross sections are higher than those by electron-impact. Cross sections by positron-impact excitation of NS, NP, and ND states, $N = 2$ to 6, are given in [17]. Cross sections for excitations to the NS states ($N = 2$ to 6) by electron impact are given in [11].

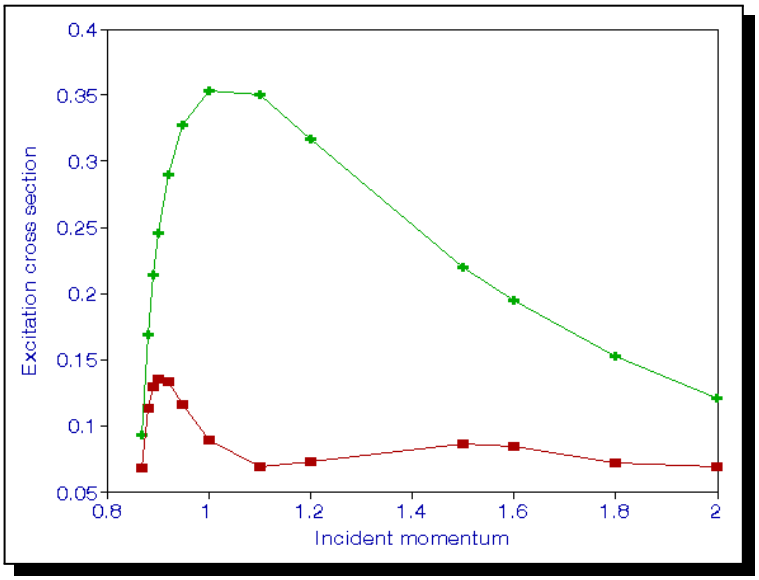

Figure 3. Excitation cross sections ((πa_0^2) of $2S$ state of atomic hydrogen by positron impact (upper curve) and electron impact (lower curve)

11. Conclusions

We have mentioned variational principles as applied to calculations of eigenvalues and continuum functions. It is important to have appropriate wave functions of the systems as in the case of H_2^+ and D_2^+. In some cases, the interaction terms should be chosen appropriately

as in the calculation of hyperfine structure of lithium. We indicated that proper formalism of scattering theory is necessary, so that it is variationally correct. Then we get phase shifts having a lower limit to the exact phase shifts. We can also then reliably assume the correctness of the continuum functions which we have used to calculate photoabsorption cross sections, as well excitation cross sections. There are lots of details which could not be given. We expect the reader to consult the original publications (references appear below). Up to now, the hybrid theory has been applied to the scattering when there is a single electron in the target. It is shown that it gives accurate results. Perhaps, it would encourage some readers to try to extend the hybrid theory to multielectron systems.

Acknowledgement

Richard J. Drachman died on April 6, 2021, in a tragic car accident. This has robbed me of his constant association and his sage advice over the years in my work, as should be evident from references given here. This paper is dedicated to him.

Competing Interests

The author declares that he has no competing interests.

Authors' Contributions

The author wrote, read and approved the final manuscript.

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