Attractive Two-Body Interactions in Partially Ionized Plasmas*

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It has recently been shown that in a classical plasma a shielded Coulomb (Yukawa) potential describes the effective two-particle interactions thorugh chains of intermediate particles. It therefore seemed reasonable to use this potential to approximate two-particle quantum interactions in a sea of charged particles, such as a hydrogen plasma. Consequently, an approximate solution of the Schrödinger equation was obtained for a hydrogen atom in a shielded Coulomb potential. With this potential, the number of H-atom bound states is finite and the energy eigenvalues are a function of the density and temperature. A variational calculation was performed using hydrogen-like single electron functions as a basis set and the effective nuclear charge as a variational parameter. Bound-state energies were obtained for 45 states of hydrogen in a grid of values for the screening constant. As the screening increases, the bound-state energy increases. For each state there is a maximum shielding above which the state is free, i.e., for which $E>0$. According to the present calculation, the energy of the ground state becomes zero at a screening of 1.15 atomic units. Above this value then, no bound states can exist.

I. INTRODUCTION AND BACKGROUND

THE calculation of the thermodynamic properties of many-body systems of charged particles, i.e., plasmas, has been given extensive study in recent years. Starting from a rigorous statistical mechanical formulation in terms of the canonical partition function, expressions for the thermodynamic functions of both classical[1,2] and quantum-mechanical[3] systems have been developed using various expansion techniques. Despite much progress, numerically useful results stemming from these methods have been scant. Only the near-classical (high temperature–low density) region and the highly degenerate (low temperature–high density) regions have been developed enough to give useful equations for one-component systems.[1-3] Hence, for the past several years, it has been the interest of the author to formulate a working model for the calculation of the thermodynamic properties of multicomponent, partially

ionized plasmas over a wide temperature-density region.[4,5] In the molecular model which has been used, the assumption is made that the total many-body system is composed of a limited number of well-chosen, few-particle subsystems which hopefully represent all those present in significant amounts in the total system. Electrons are then either free or bound to one or the other of these subsystems. Interactions which involve the free electrons are approximated by a classical ring-sum (Debye) term with a cutoff which avoids the short-range divergence. Energy eigenvalues in the partition function for the bound electronic states are obtained from solutions of the Schrödinger equation for small systems. However, the energy eignevalues of the isolated few-body systems are modified in the plasma sea and become density and temperature dependent. The success of the calculation in intermediate areas of density and temperature depends to a large extent on the model chosen to approximate these plasma-modified, few-particle interactions. In a previous model for hydrogen plasma,[5] the effect of the plasma environment on two-, three-, and four-particle interactions was approximated simply by a confinement effect. The model of an atom or moelcule in a box of variable

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[1] J. E. Mayer, J. Chem. Phys. 18, 1426 (1950); W. G. McMillan and J. E. Mayer, *ibid.* 13, 276 (1945).

[2] E. Meeron, J. Chem. Phys. 26, 804 (1957); 27, 1238 (1957); R. Abe, Progr. Theoret. Phys. (Kyoto) 22, 213 (1959); H. L. Friedman, Molecular Phys. 2, 23 (1959); 2, 190 (1959).

[3] E. W. Montroll and J. C. Ward, Phys. Fluids 1, 55 (1958); M. Gell-Mann and K. A. Brueckner, Phys. Rev. 106, 364 (1957); H. Levine, Phys. Fluids 3, 225 (1960); H. B. Levine, J. Nuclear Energy Part C, Plasma Physics 2, 206 (1961).

[4] G. M. Harris, J. Chem. Phys. 31, 1211 (1959).

[5] G. M. Harris and J. G. Trulio, J. Nuclear Energy, Part C, Plasma Physics 2, 224 (1961).

size was used and perturbed eigenvalues calculated. With this approximation, the equilibrium distribution of species varied in a qualitatively correct and fairly accurate manner.

It has now been demonstrated from a rigorous expansion of the partition function, at least for classical charged particles, that the effect of the plasma sea on localized two-particle interactions is to replace the Coulomb potential by an effective screened Coulomb potential.[2] It seemed reasonable then, that this perturbation of the quantized bound states of isolated two-particle systems would be an improvement over the "atom in a box" model for plasmas in regions where charged particles are the predominant background. Accordingly, the bound-state energies of a "hydrogen atom" in a shielded Coulomb field were calculated for the ground state and 44 excited states (through $n=9$, $l=8$) as a function of the classical Debye screening which was used in the potential. The screening is a repulsive perturbation displacing the isolated energy levels upwards and eventually into the continuum, as the Debye length becomes smaller. Then both the number of bound states and their energies are obtained as functions of the density and temperature.

There have been several previous calculations of the behavior of the hydrogen atom in a shielded Coulomb potential. The two principal ones have dealt only with "s" states and have had as a main interest an estimate of the variation of the number of bound "s" states with the screening. In a calculation made by Ecker and Weizel,[6] this relationship was obtained by an approximate analytic solution of the modified radial equation for the H atom in the limit of small shielding. The exact radial equation cannot be solved analytically and no attempt at a numerical solution was made. In an unpublished calculation of Margenau and Kelley,[7] this relationship was obtained from a variational calculation and a perturbation calculation, with slightly different numerical coefficients each time and each different from Ecker and Weizel. In the variational calculation reported,[7] unperturbed H atom wave functions were used as a basis set, with the nuclear charge as a parameter. One unperturbed function was used for each perturbed "s" state, and energy integrals were approximately evaluated. No study of the convergence properties of the variational procedure was made.

In the present calculation, a variational procedure was also used with hydrogen-like wave functions as a basis set and the exponential nuclear charge as a variational parameter. The rate of convergence of the perturbed state energies was studied for the $1s$, $2s$, and $3s$ states as a function of the number of basis set members used. The effect on the convergence of the energy for different kinds of Z variations was also studied. All

[6] G. Ecker and W. Weizel, Ann. Physik **17**, 126 (1956).

[7] D. Kelley and H. Margenau, Progress Report, October 1, 1956 (unpublished), as reviewed in H. Margenau and M. Lewis, Revs. Modern Phys. **31**, 569 (1959).

integrals involved were solved exactly. When the properties of the variational calculation were ascertained for the ground state and the $2s$ and $3s$ states, then the perturbed energies of all the remaining 42 states studied were determined by the cruder variation procedure of using only one unperturbed state per new state. This procedure is most reliable for the calculation of energies which are not too near the continuum since only bound states are used in the basis set. This means that it will be more accurate for the less excited H atom states and/or for small perturbations. The usual external check on whether the energies and number of states calculated are nearly correct cannot be made directly, since there is no simple system which is known to obey a Yukawa potential exactly. This check can be made indirectly when this model is used as part of a revised calculation of the thermodynamic properties of a hydrogen plasma. Then of course it will also be coupled with the further assumption that this entire model is a good approximation to the two-particle interactions in a plasma.

In the next section are presented the details of this calculation and in the last section results are presented and evaluated.

II. CALCULATION

The Hamiltonian for an electron interacting with a proton through a screened Coulomb potential is:

$$H = H_0 + V(r),$$

where

$$H_0 = p^2/2m, \quad V(r) = -e^2 Z(e^{-Kr})/r,$$

$K =$ reciprocal of the Debye length,

$$K^2 = 4\pi \sum_i N_i z_i^2 e^2 / VkT,$$

and $N_i =$ number of species with charge z_i.

Letting δ, a dimensionless screening parameter $= Ka_0$, then $\delta^2 = 1.0086 \times 10^{-23} \rho/kT$, where $\rho =$ density of free electron, and $kT =$ temperature in electron volts. The electronic wave function may be represented as a product of angular and radial factors. Then, since the potential is spherically symmetric, the angular parts of the Schrödinger equation can be separated out and are identical to those of the hydrogen atom. However, the resulting radial equation cannot be solved analytically and in this calculation an approximation to the eigenvalues and eigenfunctions is obtained from a variational calculation. Unperturbed H-like electronic functions were used as a basis set for the energy minimization. Because of the orthonormality of the angular parts of these functions, states with different angular momentum do not mix. Then the new eigenfunctions are expressed as linear combinations of H-atom states with the same angular momentum but different principal quantum numbers:

$$\psi_{kl} = \sum_{n=1}^{\infty} a_{knl} \Phi_{nl}(r,\theta,\varphi,Z_{knl}),$$

TABLE I. Matrix elements used to solve 3×3 secular determinant.

$$H_{11} = (Z_1^2 e^2/2a_0)[1 - 8Z_1/(\delta + 2Z_1)^2]$$

$$H_{22} = (Z_2^2 e^2/8a_0)[1 - 2Z_2(2\delta^2 + Z_2^2)/(\delta + Z_2)^4]$$

$$H_{33} = (Z_3^2 e^2/9a_0)[\tfrac{1}{2} - 4Z_3(16Z_3^4 + 216Z_3^2\delta^2 + 243\delta^4)/(2Z_3 + 3\delta)^6]$$

$$H_{12} = \left(\frac{Z_1 Z_2}{2}\right)^{\frac{3}{2}} \frac{e^2}{a_0}\left[\frac{Z_1 Z_2(4Z_1 - Z_2)}{(Z_1 + Z_2/2)^4} - \frac{(4Z_1 - 2Z_2 + 4\delta)}{(\delta + Z_1 + Z_2/2)^3}\right]$$

$$H_{13} = \frac{e^2}{a_0}\frac{1}{3}\left(\frac{Z_1 Z_3}{3}\right)^{\frac{3}{2}}\left[4Z_1 Z_3 \frac{(3Z_1^2 - 4Z_1 Z_3/3 + Z_3^2/9)}{(Z_1 + Z_3/3)^5} - \frac{(12Z_1^2 - 8Z_1 Z_3 + 4Z_3^3/3)}{(Z_1 + Z_3/3 + \delta)^4} + \frac{24Z_1\delta - 8Z_3\delta + 12\delta^2}{(Z_1 + Z_3/3 + \delta)^4}\right]$$

$$H_{23} = \frac{e^2}{3a_0}\left(\frac{Z_2 Z_3}{6}\right)^{\frac{3}{2}}\left[Z_2 Z_3 \frac{(-0.75Z_3^3 + 10Z_2^2 Z_3/3 - 5Z_2 Z_3^2/3 + 4Z_3^3/27)}{(Z_2/2 + Z_3/3)^6} - \frac{(-1.5Z_3^3 + 7Z_2^2 Z_3 - 14Z_2 Z_3^2/3 + 4Z_3^3/9 - 3Z_2^2\delta + 12Z_2 Z_3\delta)}{(Z_2/2 + Z_3/3)^5}\right.$$

$$\left. - \frac{(4Z_3^2\delta/3 + 6Z_2\delta^2 - 4Z_3\delta^2 + 12\delta^3)}{(Z_2/2 + Z_3/3)^5}\right]$$

$$S_{11} = 1$$

$$S_{22} = 1$$

$$S_{33} = 1$$

$$S_{33} = 1$$

$$S_{12} = (2Z_1 Z_2)^{\frac{3}{2}}(Z_1 - Z_2)/(Z_1 + Z_2/2)^4$$

$$S_{13} = 8(Z_1 Z_3/3)^{\frac{3}{2}}(3Z_1^2 - 4Z_1 Z_3 + Z_3^2)/3(Z_1 + Z_3/3)^5$$

$$S_{23} = 2(Z_2 Z_3/6)^{\frac{3}{2}}(-9Z_3^3 + 45Z_2^2 Z_3 - 40Z_2 Z_3^2 + 4Z_3^3)/9(Z_2/2 + Z_3/3)^6$$

where ψ_{kl} is a perturbed function with principal quantum number $n = k$ and given angular momentum l; and Φ_{nl} is an unperturbed with principal quantum nunber n and the same angular momentum as the perturbed state. When this form of the perturbed wave function is put into the eigenvalue equation, the familiar secular equation is obtained:

$$|H_{ij} - E_k S_{ij}| = 0,$$

where

$$H_{ij} = \int \Phi_i^* H \Phi_j d\tau_i d\tau_j,$$

$$S_{ij} = \int \Phi_i^* \Phi_j d\tau_i d\tau_j,$$

and i labels the n,l quantum numbers of unperturbed states. The solution of this matrix, using k basis set functions, leads to a set of perturbed eigenvalues E_k for k different linear combinations of these basis set functions. As $k \to \infty$, the lowest value of E_k approaches the ground state energy.

In practice, a small number of basis set functions were used with the exponential nuclear charge factor in each of them as an energy minimization parameter. This parameter was chosen hopefully to give rapid convergence of the energy to the correct value. First-, second-, and third-order matrices were solved for the ground-state energy and again for the energies of the 2s and 3s

states. Calculations were made using only one effective Z as a variational parameter and also using the Z in each function as a separate variation parameter. Finally, a first-order perturbation calculation was made using $Z = 1$.

Basis functions with equal values of the nuclear screening constant Z are orthogonal, but those with different values of Z are not. To do both types of variations, analytic expressions for all the matrix elements H_{ij} and S_{ij} needed were obtained and are given in Table I. These expressions were used in a 709 code which diagonalized the matrices for each point in a predetermined grid of values of the Debye shielding parameter δ. At each value of δ, the optimum energy was obtained by an iterative search for an energy minimum with respect to all Z variables. The search for a minimum energy with respect to one Z variation took an average of 10 iterations per point, while a two-Z search took about 60 and three-Z search about 150 iterations. Independent calculations minimizing the 1s, 2s, and 3s energies were made. Appendix I gives the details of the calculation of the H_{ij} matrix elements used.

The 42 remaining excited states, beyond the 2s and 3s states, were represented by a single unperturbed variational function. In this approximation then,[8]

$$H_{nl,nl}(z_{nl},\delta) = E_{nl}(Z_{nl},\delta).$$

[8] The energy is written in the form E/E_0, the fraction of bound-state energy remaining for a given value of δ (E_0 is -0.5 atomic unit for 1s). This fraction is positive until the energy crosses zero and the state becomes unbound.

TABLE II. Ground-state energies in different approximations.[a]

E/E_0 δ	a	b	c	d	e
0	1	1	1	1	1
0.05		0.90363	0.90363	0.90363	0.90363
0.15		0.73086	0.73089	0.73089	0.73092
0.25	0.58024	0.58149	0.58168	0.58171	0.58183
0.30		0.51465	0.51498	0.51504	0.51527
0.40		0.39515	0.39604	0.39618	0.39675
0.50	0.2802	0.29301	0.29490	0.29516	0.29623
0.60		0.20671	0.21018	0.21060	0.21266
0.70		0.13500	0.14088	0.14145	0.14366
0.75	0.05780	0.10431	0.11182	0.11240	
0.80	0.0202	0.07694	0.08639	0.08692	0.08940
0.828	0	0.0625			
0.90		0.30194	0.04615	0.04634	0.04860
0.95		0.01428	0.03101	0.03103	0.03298
1.00		0	0.01880	0.01887	0.02045
1.05		−0.0104	0.0092	0.0097	0.01091
1.10			0.00194	0.00342	0.00423
1.15			−0.00304	−0.000418	0
δ_0	0.828	1.00	1.13	1.14	1.15
δ_i		1.06	1.15	1.17	1.15

[a] a is a first-order perturbation calculation for $Z=1$; b is a first-order variational calculation varying one Z; c is a second-order variational calculation varying one Z; d is a third-order variational calculation varying one Z; e is a third-order variational calculation varying three Z's. $E_0 = -0.5$ atomic units (a.u.).

For this part of the calculation it was no longer practical to calculate the matrix elements by hand and use them as input for the matrix diagonalization computation. Since a large number of excited states were computed, a code was written to generate expressions for the diagonal elements needed. The method used to do this is given in Appendix II. Using these expressions then, each state energy was varied to a minimum with respect to the nuclear charge paramteer Z using a direct search procedure at each value of δ selected.

III. RESULTS

A. Convergence Properties of the Variational Procedure

1. Ground State Calculation

The energy of the $1s$ state as a function of the screening parameter δ, is given in Table II for five calculations of differing approximation: a first-order perturbation calculation with effective $Z=1$; a first-, second-, and third-order variational calculation using only one Z for a variational parameter; and a third-order calculation varying all three Z's independently. Because the true energies of this system are not known, the error in these calculations cannot be directly stated. However, results can be compared for relative reliability:

(a) Comparison of the two first-order calculations indicates that a very significant energy lowering is obtained by allowing the effective nuclear charge to vary from the isolated atom value to a value which minimizes the energy.

(b) The improved energy obtained by adding the contribution of the $2s$ state to the $1s$ state becomes

significant (i.e., $>0.5\%$) at a $\delta=0.50$ and rises to greater than 100% just before the state becomes free. The energy difference is less than 10% for energies down to 10% of the unperturbed value

(c) The energy improvement by adding a third configuration, the $3s$ state, to the ground state is less than 0.5% over the range of δ until the energy is reduced to less than 0.01 of its original value. This percent change is in general about a factor of 10–15 less than the difference between the first- and second-order calculations. Thus convergence is rapid enough that no more than a 3×3 matrix need be solved for four-figure precision, except for values of $\delta\geq0.95$ and of $E/E_0\leq0.03$.

(d) For a third-order matrix and larger, significantly more energy lowering is obtained by varying the effective nuclear charge parameter in each wave function than by increasing the number of configurations used with only a one-Z variation. Then for matrices higher than third order there should be more than one variational parameter.

(e) The higher the calculated bound-state energies, the lower the calculated value of the shielding (δ_0) at which the state becomes unbound. For example, the value of δ_0 from the first-order variational calculation of the ground-state energy is 15% lower than that obtained for the 3×3 calculation varying three parameters. This latter, most accurate value of δ_0 is probably within 1% of being correct.

(f) When the bound-state energy becomes positive, the form of the wave function changes to a free electron function. In practice, in this calculation, for some value of $\delta_i > \delta_0$ shortly after E becomes zero, a real positive Z which minimizes the energy can no longer be found. The closer the coincidence of these two points, the better the wave function is in this respect. As can be seen from Table II, these two points coincide for the most accurate calculation and differ by 6% for the first-order variational calculation.

2. Excited States; 2s and 3s

Table III gives the energy of the $2s$ state as a function of the screening parameter for the same five calculations as were done for the ground state. Similar calculations

TABLE III. Energy of $2s$ state for various approximations.

E/E_0[a] δ	a	b	c	d	e
0	1	1	1	1	1
0.05	0.65350	0.655	0.65400	0.65412	0.65414
0.10	0.39330	0.40024	0.39764	0.39900	0.39942
0.15			0.21127	0.21680	0.21773
0.20	0.04176	0.10643	0.0817	0.0961	0.0965
0.25	−0.0786		0.00074	0.0253	0.0257
0.30		0.02148	−0.00082	−0.09665	0
0.40		0			
δ_0	0.225	0.40	0.28	0.28	0.30

[a] $E_0 = -\frac{1}{8}$ a.u.

TABLE IV. Comparison of energies from ground-state and excited state minimization.[a]

| | E_{1s} | | | | E_{2s} | | | | E_{3s} | | |
δ	a	b	c	δ	a	b	c	δ	a	b	c
0.1	−0.4070	−0.4068	−0.3898	0.1	−0.04981	−0.04988	−0.04575	0.1	+0.00138	+0.0005	−0.00193
0.15	−0.3655	−0.3649	−0.2651	0.15	−0.02698	−0.02710	0	0.15	+0.01431	+0.01169	0
0.20	−0.3268	−0.3261		0.20	−0.01194	−0.01201					
0.25	−0.2908	−0.2894		0.25	−0.00306	−0.003157					

[a] a is the 3 ×3 diagonalization minimizing 1s energy; b is the 3 ×3 diagonalization minimizing 2s energy; c is the 3 ×3 diagonalization minimizing 3s energy.

were made for the 3s state. The energy of the 2s and 3s states were found by minimizing each with respect to the Z parameters in separate calculations rather than taking the energy of the orthogonal partners of the ground state as the excitation energy. Table IV compares the energies obtained for the 1s, 2s, and 3s states when each of these energies was minimized in turn. The improvement in the 2s state energy ranges from only 0.14% at a δ of 0.1 to 3% at a δ=0.25, just before it becomes unbound. There was no appreciable difference in the value of δ_0, which was 0.28 for both cases. The energy of the 3s state was improved appreciably, when it rather than the 1s state energy was minimized. The value of δ_0 was at the same time increased from <0.1 to 0.15.

From Table III, it is seen that of the two first-order calculations, the variational one gives the lower energy as it did for the ground state. However, here the 1×1 variational energy is *lower* than the 2×2 and 3×3 energy. This is because minimization of the energy of an excited state using a single variation function gives an energy which is neither an upper nor lower limit of the true energy of the system. Only if a matrix of order ≥2 is diagonalized is the resulting energy value an upper limit of the true value. For the 2s state, not much energy lowering is obtained in going from a second- to a third-order calculational or from one 3×3 to the other. Yet the 1×1 energies are considerably lower than any of these which are upper limits of the true energy. Therefore it is very likely that, for the excited states, energies calculated from a single variational function are lower than the true value. Then, values of δ_0 obtained from the first-order calculations are too high, and those from the others are too low. This places the true value of δ_0 for the 2s state between 0.28 and 0.4 and for the 3s state between 0.15 and 0.28.

B. Excited States as Single Variational Functions: Bound-State Energies and Continuum Conditions

Table V gives the energies of the excited states through principal quantum number 9. These results were obtained by minimizing a single variational function per excited state. As the screening increases the
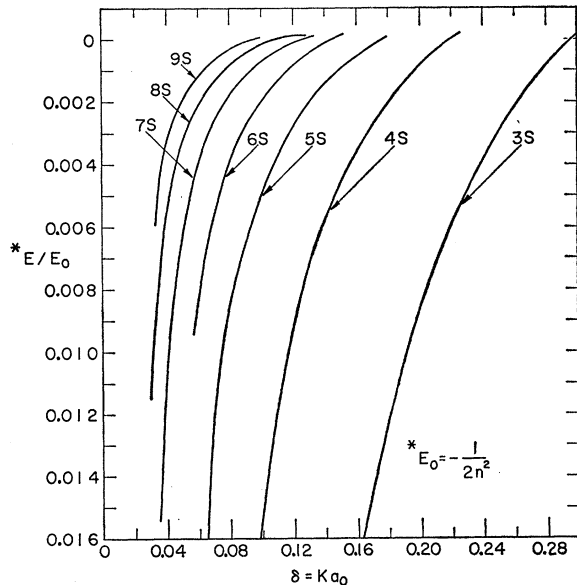

FIG. 1. Energy of excited s states as a function of screening n=2−9.
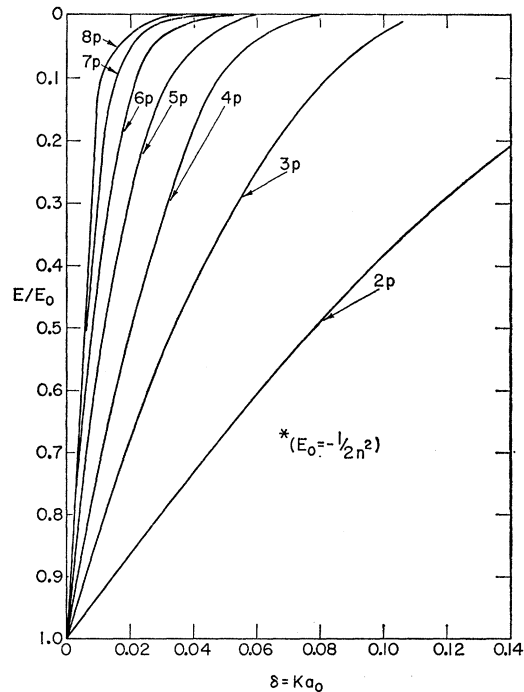

FIG. 2. Energy of p states n=2−8.

TABLE V. Excited state energies.

E/E_0 \ δ	3s	4s	5s	6s	7s	8s	9s	2p	3p	4p	5p
0	1	1	1	1	1	1	1	1	1	1	1
0.02	0.6844	0.4928	0.3046	0.1516	0.0573	0.0157	0.0209	0.8800	0.6832	0.4886	0.2982
0.04	0.4453	0.1975	0.0565	0.0216	0.01078	0.0060	0.00357	0.7369	0.4358	0.1822	3.98×10^{-3}
0.06	0.2699	0.0635	0.0190	0.00827	0.00410	0.0022	0.00123	0.6073	0.2492	0.03800	2.96×10^{-4}
0.08	0.1492	0.02715	0.0083	0.00397	0.00183	0.00086	0.00037	0.4905	0.1166	0.00223	0
0.10	0.07642	0.01520	0.00515	0.00198	0.00074	0.000107	-0.000034	0.3855	0.03855	0	
0.12	0.04134	0.00930	0.00289	0.00086	0.000114	0.000063		0.2918	-0.0274		
0.14	0.0260	0.00585	0.00148	0.00016	-7.7×10^{-5}			0.2090			
0.16	0.0176	0.00360	0.00052	-0.00014				0.1366			
0.18	0.0123	0.00202	-0.00010					0.0747			
0.20	0.00864	0.00085						0.0233			
0.22	0.00591	-1.6×10^{-5}						-0.01652			
0.30	-0.0002										

E/E_0 \ δ	6p	7p	8p	9p
0	1	1	1	1
0.01	0.4433	0.3111	0.2052	0.1264
0.020	0.14334	0.0528	0.0294	0.018
0.030	0.0333	0.0120	0.00487	0.0034
0.035			0.000081	-4.6×10^{-5}
0.04	0.00973	0.00247		
0.045		-0.0002		
0.05	0.00172			

E/E_0 \ δ	3d	4d	5d	4f	5f
0	1	1	1	1	1
0.01	0.6753	0.478	0.2844		
0.020	0.4133	0.1512	0.00837	0.4635	0.2645
0.030	0.2070	-0.0873	0		
0.035	0.0532			0.1065	
0.04	0			0	0

E/E_0 \ δ	6d	7d	8d	9d
0	1	1	1	1
0.005	0.4377	0.3039	0.1868	0.1048
0.008	0.3577	0.2207	0.1067	0.0427
0.010	0.287	0.1536	0.0544	0.00162
0.012	0.2252	0.1006	0.0254	-0.00305
0.014	0.1269	0.0361	0.0098	
0.016	0.0110	-0.00158		
0.017	-0.0014			

E/E_0 \ δ	6f	7f	8f	9f
0	1	1	1	1
0.01	0.430	0.5842	0.4856	0.3930
0.012		0.2939		
0.020			0.1745	0.0814
0.030			0.0978	0.0086
0.035	0.1027	0.01236	0.0153	-0.0222
0.04	-0.00827	-0.00189	-0.00208	

E/E_0 \ δ	5g	6g	7g	8g	9g
0	1	1	1	1	1
0.005	0.2384	0.677	0.5803	0.4808	0.3827
0.01	0	0.419	0.2807	0.1600	0.0688
0.012				0.0787	0.01425
0.020		0.0713	-0.00516	-0.0065	-0.00037
0.024		-0.00761			

E/E_0 \ δ	6h	7h	8h	9h	7i	8i	9i	8j	9j	9k
0	1	1	1	1	1	1	1	1	1	1
0.005	0.673	0.5754	0.4746	0.3747	0.5695	0.4673	0.3661	0.4589	0.3561	0.3447
0.01	0.506	0.376	0.254	0.1470	0.3630	0.2378	0.1288	0.2194	0.1079	0.0845
0.012	0.406	0.2644	0.1409	0.0481	0.2452	0.1186	0.0241	0.0930	-0.0029	-0.0325
0.013	0.315	0.1684	0.0545	-0.0078	0.1429	0.0264	-0.0011	-0.0055		
0.016	0.232	0.0879	-0.0045		0.0564	-0.0009				
0.019	0.159	0.02331			-0.0132					
0.020	0.123	-0.0026								
0.024	0.03317									
0.04	-0.0149									

TABLE VI. Maximum value of screening factor for each bound state.

$\backslash^{\delta_0}$ n $\backslash$ s		p	d	f	g	h	i	j	k
1	1.15								
2	0.40	0.210							
3	0.295	0.110	0.090						
4	0.220	0.080	0.050	0.050					
5	0.177	0.060	0.040	0.035	0.030				
6	0.145	0.052	0.034	0.027	0.023	0.021			
7	0.126	0.046	0.029	0.021	0.018	0.017	0.0155		
8	0.108	0.040	0.025	0.018	0.016	0.013	0.0125	0.0115	
9	0.094	0.035	0.0145	0.012	0.012	0.011	0.0105	0.0100	0.0095

energy increases more and more slowly, approaching zero asymptotically. This leveling off near zero energy is more pronounced for states with higher principal quantum number. Examples of the energy variation are shown in Figs. 1 and 2 for the s and p states, respectively.

In this approximation, states of different l and n quantum numbers do not mix and do not cross. However, the "l degeneracy" of the isolated hydrogen atom is broken. This may be observed in Fig. 3 where the energies of states with princpal quantum number 6 are plotted.

Judging from the results of the calculations for the $2s$ and $3s$ states, the energies of all excited states calculated here are most probably low. In addition, as was expected from the inaccuracies mentioned in the ground-state calculations, excited states with less than 1/100 of the energy of the ground state gave completely unreliable results. Then, for a principal quantum number ≥ 10, this approximation to the perturbed states breaks down at essentially zero perturbation.

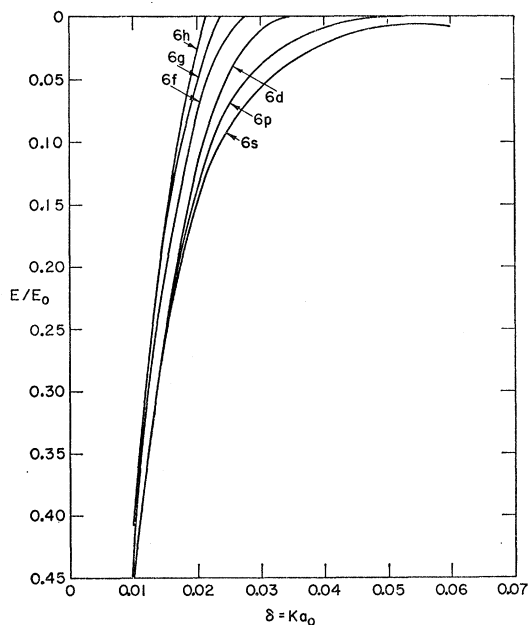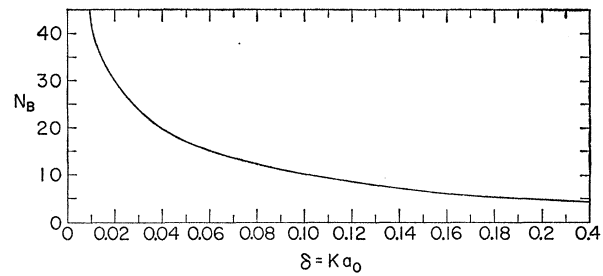Table IV gives the value of the screening parameter

FIG. 3. Splitting of l degeneracy for $n=6$ states.

FIG. 4. Number of bound states as a function of screening.

for which each state energy is zero. From this data, the variation in number of bound states with screening length is plotted in Fig. 4. It appears that as the screening goes to zero, the number of bound states approaches infinity asymptotically.

C. Comparison of Numerical Results

For the s states, comparison of the values of δ_0 calculated here and from previous work can be made. The approximate analytic calculation of Ecker and Weizel[6] (EW) led to the relationship: $g^{*2}=z/\delta$, where g is the highest principal quantum number of an s state which is still bound at a screening of δ. The perturbation calculation of Margenau and Kelly[7] (PMK) led to the expression $g^{*2}=0.86\ z/\delta$; while their variational calculation (VMK) gave the result: $g^{*2}=0.804\ z/\delta$. Table VII gives the values of δ calculated from these formulas and from the present work. For the $1s$, $2s$, and $3s$ states, the value of δ_0 obtained here from the 3×3, 3-parameter calculations, must be the most accurate. Ecker and Weizel's calculation seems to give an answer for the $1s$ state equivalent to the present first-order variational results. The two first-order perturbation calculations, PMK and the present one, are comparable and give a still worse value of δ_0. For the ground state, the worst value of δ_0 is the VMK one. For the excited states, values of δ_0 from the present first-order variational calculation are much higher than any of the others. The large discrepancy between the unpublished VMK results and the present ones is sur-

TABLE VII. Comparison of δ_0 values for nine "s" states.

State	EW[a]	PMK[a]	PH[a]	VMK[a]	VH$_1$[a]	VH$_3$[a]
$1s$	1	0.86	0.83	0.804	1.00	1.15
$2s$	0.25	0.215	0.215	0.210	0.40	0.28
$3s$	0.111	0.095	0.095	0.089	0.295	0.15
$4s$	0.062			0.052	0.22	
$5s$	0.04			0.032	0.177	
$6s$	0.0278			0.022	0.145	
$7s$	0.0204			0.016	0.126	
$8s$	0.0156			0.0125	0.108	
$9s$	0.01234			0.0099	0.094	

[a] EW =Ecker and Weizel calculation (reference 6); PMK =Margenau and Kelley perturbation calculation (reference 7); PH =present perturbation calculation; VMK =Margenau and Kelley variational calculation (reference 7); VH$_1$ =present single function variational calculation; VH$_3$ =present (3×3) variational calculation.

TABLE VIII. Region of applicability of shielding for 45 bound states.

V (cc/mole)	$(N_e/kT)_{min}$[a]	$(kT)_{min}$[b]	$(kT)_{max}$	$(N_e)_{min}$[c]	$(N_e)_{max}$[d]	δ for $N_e = 1\%$[e]
12000	1.592×10^{-1}	1.75	6.0	25%	95%	0.002
6000	7.962×10^{-2}	1.5	12.5	8.5	98	0.003
3000	3.981×10^{-2}	1.5	25	6.3	99	0.005
1200	1.592×10^{-2}	1.5	60	4.25	100	0.007
600	7.962×10^{-3}	1.0	125	0.80	100	0.01
400	5.308×10^{-3}	1.0	185	0.53	100	
120	1.592×10^{-3}	1.0	625	0.16	100	
60	7.962×10^{-4}	1.0	1250	0.080	100	
30	3.981×10^{-4}	1.0	2500	0.040	100	
12	1.592×10^{-4}	1.0	6250	0.016	100	
6	7.962×10^{-5}	1.0	12500	0.008	100	
3	3.981×10^{-5}	1.5	25000	0.012	100	
1.5	1.990×10^{-5}	2.0		0.008	100	

a $(N_e/kT)_{min} = (N_e/kT)\delta = 0.009 = 1.327 \times 10^{-5} V$, since $\delta^2 = 6.101 N_e/VkT$, where N_e =fractional ionization, V =volume/mole, and kT =temperature in electron volts.
b kT is the temperature in electron volts.
c $(N_e)_{min}$ =percent ionization when shielding is turned on.
d $(N_e)_{max}$ =percent ionization where shielding is turned off.
e $\delta^2 (N_e = 1\%) = 6.101 \times 10^{-2}/V$.

prising, since presumably a very similar single-function variational procedure was used. Since using a single function can give energies that are either too high or too low, it seems apparent that the present results give values that are too high and previous ones give values that are too low.

D. Use of a Shielded Coulomb Potential in a Plasma

1. Region of Applicability

Having obtained the energy of isolated two-particle bound states perturbed by a shielding of the Coulomb potential, the question arises as to the density-temperature regions for which it is an apt model for two-particle interactions in plasmas. In general, it should be applicable for a partially ionized plasma where the number of both bound and free particles is significant. However, as the shielding approaches zero (the Debye length gets large) this perturbation becomes less important while the number of bound states that must be considered in the calculation increases. Therefore this model should be used with a cutoff value of δ, a minimum significant shielding. Perturbations of two-particle states at lower values of the shielding could then be approximated by neutral particle interactions, with care taken to insure a smooth counting of states and energy variation when considering both neutral and charged particle perturbations of the bound states.

From the results of the present calculation using 45 states, the minimum value of δ that could be used is 0.009 and the maximum value when the last state disappears is 1.15. To translate this range of shielding to a usable temperature-volume grid, use was made of the percent ionization figures obtained from a previous calculation.[6] For each of a series of volumes ranging for hydrogen from a standard gas to a tenfold compressed solid, minimum values of N_e/kT corresponding to $\delta = 0.009$ were translated to a useful temperature range. These are given in Table VIII. The percent

ionization when the perturbation is turned on and off is also given in the table. If it is reasonable to consider the shielding perturbation to be significant for $N_e \geq 1\%$, then it is estimated from the figures of Table VIII that 45 excited states could be used in a calculation of the thermodynamic properties of a hydrogen plasma for volumes ≤ 750 cc/mole and temperatures from room temperature to the region of complete ionization.

2. Critique of the Energy Criterion for Bound States

Instead of an energy criterion for the definition of a bound state, i.e., as one with $E < 0$, a size criterion could possibly be used. That is, it might be decided that a state is no longer bound if its average radius exceeds the average internuclear separation at a given density and temperature. An analysis was made of the present results to see how these two criteria agree. The average radius of a hydrogen-like electronic state is: $\langle r_{nl} \rangle = a_0 [3n^2 - l(l+1)]/2z_{nl}$. From a calculation of the average radii for each of the 45 states, it is concluded that for values of δ for which the state is still bound there corresponds some specific volumes for which the state would not fit. Therefore these two criteria do not mesh and there is an appreciable density-temperature region for each state when it is considered bound but does not "fit" into the volume occupied on the average solely by one proton. The error being made then is to still consider the electron as bound exclusively to one proton when it overlaps appreciably onto one or more additional nuclei. At that point threee-, four-, and more-particle bound states should really be considered.

For the model of the bound-state perturbation as atoms in a box, there were also some states with $E < 0$ which did not fit into the average specific volume of the system. If the size criterion had been used, then the bound states would have cut out at lower densities. With the shielded Coulomb perturbation of the bound states, the H-atom states stay gound even longer than they do for the atom in a box, thus increasing the dis-

parity between the size and energy criterion. However, in some intermediate density-temperature regions (roughly $1 < T < 5$ ev, $12 < V < 120$ cc/g) this more gradual disappearance of bound states is just the correction needed to improve the model. The atom in a box model, because of the more rapid disappearance of states, gave too high a volume derivative of the free energy and therefore too high a pressure.

The present model, then, does show some promise of giving reasonable thermodynamic properties in the very difficult intermediate regions of density and temperature for a partially ionized plasma.

ACKNOWLEDGMENTS

APPENDIX I

The matrix elements for the Hamiltonian used in the diagonalization and minimization routines were calculated as follows:

$$H_{ij} = A\left[\int_0^\infty \varphi_i^*(r) T \varphi_j(r) r^2 dr \right.$$
$$\left. + \int_0^\infty \varphi_i^*(r) V(r) \varphi_j(r) r^2 dr \right] = A(T_{ij} + V_{ij}),$$

where A = numerical factor from the angular integration, T = kinetic energy operator, and V = potential energy. To calculate T_{ij}, use was made of the fact that the φ_i's are eigenfunctions of the equation:

$$(T - Z_j e^2/r)\varphi_j(r) = (-Z_j e^2/2a_0)\varphi_j(r).$$

Then

$$T_{ij} = Z_j e^2 \int_0^\infty (\varphi_i^* \varphi_j/r) d\mathbf{r}_i d\mathbf{r}_j - Z_j e^2/2a_0\left(\int_0^\infty \varphi_i^* \varphi_j d\mathbf{r}_i d\mathbf{r}_j \right).$$

The potential energy integral is of the form:

$$V_{ij} = -e^2 \int_0^\infty \varphi_i^* \varphi_j (e^{-Kr}/r) d\mathbf{r}_i d\mathbf{r}_j.$$

The H-atom-like wave functions used were:

$$\varphi_{1s} = (1/4\pi)^{\frac{1}{2}}(Z_1/a_0)^{\frac{3}{2}} 2 \exp(-Z_1 r/a_0),$$

$$\varphi_{2s} = (1/4\pi)^{\frac{1}{2}}(Z_2/2a_0)^{\frac{3}{2}}(2 - Z_2 r/a_0) \exp(-Z_2 r/2a_0),$$

$$\varphi_{3s} = \tfrac{1}{3}(4\pi)^{-\frac{1}{2}}(Z_3/3a_0)^{\frac{3}{2}}[6 - 4Z_3 r/a_0 + (2Z_3 r/3a_0)^2]$$
$$\times \exp(-Z_3 r/3a_0).$$

When these functions were substituted into the expressions for T_{ij} and V_{ij} all integrals obtained could be expressed in terms of gamma functions and were easily evaluated.

APPENDIX II

The diagonal elements of the Hamiltonian used for the 1×1 calculation of the excited state energies were generated by a recursion formula developed in the following way: Let

$$H_{ii} = H_{nl} = T_{nl} + V_{nl},$$

$$T_{nl} = Z_{nl}^2/2n^2,$$

$$V_{nl} = \int_0^\infty R_{nl}^*(r) V(r,\delta) R_{nl} r^2 dr$$

$$= -e^2 \sum_{k=0}^{n-l-1} \sum_{k'=0}^{n-l-1} \frac{(n-l-1)!(-1)^{k+k'}[(n+l)!]^4(2Z/na_0)[2Z/(2Z+n\delta)]^{2l+k+k'+2}(2l+k+k'+1)!}{2n(n+l)!^3(n-l-1-k)!(n-l-1-k')!(2l+1+k)!(2l+1+k')!k!k'!}$$

$$= \frac{-e^2 Z}{n^2 a_0} \sum_{k=0}^{q} \sum_{k'=0}^{q} \frac{q!(-1)^{k+k'}(q+s)!x^{2l+2+k+k'}(s+k+k')!}{(q-k)!(q-k')!(s+k)!(s+k')!k!k'!},$$

where $s = 2l+1$, $q = n-l-1$, and $x = 2Z/2Z + n\delta$. Let $k+k' = t$, then

$$V_{nl} = \frac{-e^2 Z x^{2l+2}}{n^2 a_0}\left[\sum_{t=0}^{q}\sum_{k=0}^{t} + \sum_{t=q+1}^{2q}\sum_{k=t-q}^{q}\right]\frac{q!(q+s)!(-x)^t(s+t)!}{(q-k)!(q-t-k)!(s+k)!(s+t-k)!k!(t-k)!}.$$

Let

$$A_{tk} = \frac{q!(q+s)!(s+t)!}{(q-k)!(q-t+k)!(s+k)!(s+t-k)!k!(t-k)!};$$

then

$$V_{nl} = \frac{-e^2 Z x^{(2l+2)}}{n^2 a_0} \left[\sum_{t=0}^{q} \sum_{k=0}^{t} + \sum_{t=q+1}^{2q} \sum_{K=t-q}^{q} \right. \left[A_{tK}(-x)^t. \right.$$

A table of coefficients A_{tK} was generated by the following procedure: Using

$$A_{00} = (q+s)!q!s! = \frac{(n+l)!}{(n-l-1)!(2l+1)!} = n \sum_{j=1}^{l} \frac{(n^2-j^2)}{2j(2j+1)},$$

a value of A_{00} is calculated and from it coefficients A_{t0} generated, using

$$A_{t+1,0} = A_{t0}(q-t)/(t+1).$$

Then for each t, A_{tK} was determined using

$$A_{t,K+1} = A_{tK}(q-K)(s+t-k)(t-k)/(q-t+k+1)(s+k+1)(k+1),$$

up to $t=q$. Coefficients with $t>q$ of the form $A_{q+1,1}$, $A_{q+2,2}$ were generated from $A_{q,0}$ by the following formula:

$$A_{t+1,(k=t-q+1)} = A_{t,(k=t-q)}(2q-t)(s+t+1)/(s+t-q+1)(t-q+1),$$

with k advanced in steps from 0 to q. The potential energy integral U_{nl} could then be calculated from the table of A_{tk} by summing over K, multiplying by $(-x)^0$ for each value of x and t, and finally summing over t.