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Classical Models and Many-Electron Atoms

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Based on classical models including the interpretation of the deBroglie wave as an electromagnetic "atmosphere" which controls the orbit and the "action" of the classical electron, and postulating that the "atmosphere" of the electron suffers a permanent change only when the electron undergoes a change in its quantum state, an equation is derived for the He ground state *iso*-electronic sequence which agrees substantially with experiment. This view leads to the conclusion, moreover, that the binding energy in molecules formed without electronic transitions is caused entirely by a decrease in the average potential energy, the average kinetic energy of the molecule remaining the same as in the constituent atoms. This conclusion is verified in the systems H_2 and H_2^+ . Introducing the additional assumption that the resonance contribution to the total energy of a state, arising from an "adiabatic" orbital distortion, is proportional to the orbital frequency, equations are derived expressing the term values of a number of states of two-, three-, and four-electron atoms. The methods appear to apply quite generally.

IN a recent article¹ it was shown that the molecules H_2 and H_2^+ may be treated with good accuracy by classical models and old quantum theory employing in addition a concept of resonance. The purpose of this discussion is to apply similar methods in the calculation of energy states (ground and excited) of several many-electron atoms. In dealing with classical models in light of present knowledge one quite naturally is led to adopt an interpretation of the wave characteristics of matter similar to the views held by Thomson,² Schott,³ Japolsky⁴ and others, namely, that the wave associated with the electron is simply an electromagnetic "atmosphere." The chief concern here is to justify the stationary states, i.e., the non-radiation of the field of the accelerating charged particle. Schott proved with Maxwell's equations that non-radiating orbits of charged particles are indeed possible although he was not able to account for the Bohr orbits of hydrogen. One may wonder perhaps what part the nucleus plays in the non-radiation of the field of the electron in its stationary orbits.⁵ It seems not altogether impossible, when we realize that the deBroglie

wave-length of the proton would be the same as that of the electron in the classical model of hydrogen, that the Poynting vector may be nullified by an over-lapping of opposite fields when the boundary conditions are satisfied. At any rate there does not seem to be any very good reason in electromagnetic theory for discounting the possibility of standing light waves surrounding the elementary charged particle. On the other hand, this postulate certainly allows a clearer comprehension of the control of the orbit by conservation of energy, and even of the underlying meaning of quantum states. We visualize the "atmosphere" as not only providing the control of the orbit but of being the source of the "action," i.e., the momentum of the particle. In this view there is no mysterious condensation of field to ponderable matter, but the light quantum, when it is absorbed by matter, merely superimposes itself on the "atmosphere" already present. However these matters, while of philosophical interest, are important only when in serving as basic postulates they allow us to make further progress in the interpretation of the laws of nature.

KINETIC VS. POTENTIAL ENERGY IN SYSTEMS WITH RESONANCE

According to the virial theorem the total energy of systems operating under inverse square forces alone is equal to the negative of the average kinetic energy (\bar{T}), or to half the average

¹ M. A. Cook, J. Chem. Phys. **13**, 262 (1945).

² J. J. Thomson, Phil. Mag. [7] **5**, 191 (1928); **6**, 254 (1928); **8**, 1073 (1929); **9**, 1185 (1930); **12**, 1057 (1931); **16**, 809 (1933); **27**, 1 (1939).

³ G. A. Schott, Proc. Roy. Soc. (London) **A139**, 37 (1933); **A171**, 1 (1939).

⁴ N. Japolsky, Phil. Mag. **20**, 417, 641 (1935); **22**, 1003 (1936).

⁵ W. M. Hicks, Phil. Mag. [7] **8**, 108 (1929).

potential energy (\bar{V}). However, as shown by Slater,⁶ the vibrating nuclei in molecules have the effect of applying a (non-Coulombic) constraint at any nuclear separation other than the (static) equilibrium one. Moreover, it was shown¹ that the true (dynamical) equilibrium distance in H_2 and H_2^+ differs widely from the static equilibrium position. Thus, in the circular model of H_2 with rigid nuclei, R (the internuclear distance) turns out to be .58A, but the true value is .74A. As a consequence it is found that $\bar{T} \neq -E \neq -1/2\bar{V}$. Slater pointed out in fact that the binding energy in molecules seemed to be caused largely (it appears from our analysis, entirely) by a decrease in \bar{V} . This is of course contrary to the considerations of Hirschfelder and Kincaid⁷ who evaluated the various treatments of H_2 on the basis that a correct solution should give $\bar{T} = -1/2\bar{V}$.

Now the wave-length of the particle, according to deBroglie, is a function of the classical momentum, and a change in momentum must accordingly be accompanied by a change in the wave-length. By our interpretation of the deBroglie wave as a peculiar type of electromagnetic "atmosphere," this seems to imply an absorption or emission of radiation whenever \bar{T} undergoes a change. However, no such radiation occurs in the formation of most molecules, e.g., H_2 from two H atoms; it is necessary for the H atoms to lose energy to a suitable third body before they will form the molecule. We suspect, therefore, that there may be no change in \bar{T} in the "adiabatic" formation of the molecule from its atoms. We recognize that the foundation of this postulate may seem to conflict with the fact that the binding energy will to a large extent appear as kinetic energy (translational) in other systems. It is true also that if resonance exists between the various particles of the system there must be a corresponding resonance interchange of field between the particles as required by the deBroglie formula. However, let us re-examine the H_2 and H_2^+ solutions of reference (1) to see if it may be verified that the average kinetic energy remains constant in molecular formation.

From Eqs. (2) and (3) of reference (1), it will

be seen that $RF = 1/2RF_1$, since $\bar{T} + 1/2\bar{V} = -1/2RF = -1/4RF_1$. This is apparent also from the fact that $RF_2 = 0$ as seen by Eq. (3b). Thus $RF = 1/2g\epsilon^2/\bar{r}$ at the equilibrium distance R , where \bar{r} is the root mean square average of r_1 and r_2 . Since $\bar{T} = -E - RF$, we thus have $\bar{T} = -E - 1/2g\epsilon^2/\bar{r}$. Employing the values of r_1 and r_2 in reference (1) corresponding to $R = 1.06A$ and .74A, we obtain for \bar{T} the values 13.39 and 26.77 ev for H_2^+ and H_2 , respectively. (In the case of H_2 it was assumed as in reference (1) that $\theta = \phi$ at $R = .74A$.) These values differ from the expected ones by almost exactly the vibrational energy which would be entirely kinetic at the equilibrium position. Hence, as expected, the average kinetic energy of these molecules is at least approximately the same as in the corresponding constituent atoms.

If as a general rule, then, we postulate that \bar{T} remains unchanged in the "adiabatic" interaction of atoms to form molecules so far as the internal energy is concerned, we conclude that the binding energy in molecules formed without change in the electronic configuration is caused entirely by a decrease in \bar{V} . This is an interesting consideration if true. In fact, if it can be justified, it would provide a very valuable principle in the study of molecules, the interaction of light and matter, and in other problems. It thus becomes of interest to extend the postulates to other resonance systems. In a restricted sense the same sort of thing is involved in the structure of many electron atoms as in molecules. That is, as a second electron enters an atomic system, the orbital of the first one must suffer a distortion caused by the electron-electron interaction. This would be "adiabatic" in the same sense as in molecules since it involves no change in the quantum numbers of the first electron.

TWO-ELECTRON ATOMS (GROUND STATES)

We shall adopt a modified circular model for this system similar to that employed in H_2 . It is evident, however, that the model must be somewhat different in this case as the resonance phenomenon must be different in character from that found in molecules, the latter being associated to a large extent with nuclear vibrations. If there were no resonance or exchange energy involved, the ground state energy of two-electron

⁶ J. C. Slater, J. Chem. Phys. 1, 687 (1933).

⁷ J. Hirschfelder and J. Kincaid, Phys. Rev. 52, 658 (1937).

TABLE I. Ground states of helium and helium-like atoms (ev).

Atom	$-E$ ($k=.725$)	$-E$ (obs.)
H ⁻	14.29	
He	(78.61)	78.61
Li ⁺	197.07	197.10
Be ²⁺	369.70	369.75
B ³⁺	596.46	596.59
C ⁴⁺	877.38	877.67

atoms according to the circular model would be given by the equation

$$E' = -(4Z-1)\epsilon^2/4r = -(4Z-1)^2 Rhc/8, \quad (1)$$

with $r=4a_0/(4Z-1)$ for the coincident orbital radius, the other quantities having their usual significance. We consider the circular model to be merely transitory in the dynamic structure of the atom, representing an equilibrium structure as in H₂. The energy in (1) is, therefore, dashed to show that it is not the true value. According to the above postulate at the configuration where the circular model applies there should be an additional energy (the resonance energy) to account for the "adiabatic" change or distortion of the original one-electron orbit. That is, we consider that radiation takes place only from the field of the second electron entering the system, and that there should thus be an additional kinetic energy given by

$$T' = \frac{1}{2} \int_{r_0}^r (Z-k)\epsilon^2/r^2 dr, \quad (2)$$

where r and r_0 are the radii of the coincident two-electron and the original one-electron orbits, respectively, and k is a factor accounting for the electron-electron interaction. The factor $\frac{1}{2}$ accounts for the fact that we are dealing with kinetic energy, the integral being of the form of a potential energy term. We shall leave k undetermined, noting that it is of the same form as Z , and therefore is the same for all members of the sequence. Hence the arbitrary assignment of any value for k should give values for E ($=E'+T'$) for the normal He *iso*-electronic sequence which differ from the true values by a constant amount plus the spin and relativity corrections, the integral (2) turning out to be a constant ($Rhc/4$) times $Z-k$. Hence,

$$E = E' + T' = [2(Z-k) - (4Z-1)^2] Rhc/8. \quad (3)$$

Table I shows values of E obtained from (3) for $k=.725$, the value needed to give agreement with experiment in normal He. It is seen that the agreement is about what should be expected with spin and relativity contributions neglected. This treatment does not of course give the detailed mechanism of the resonance effect although one might guess that it involves orbital pulsations and/or oscillations through the coincident circular model orbit as an equilibrium position.

EXCITED STATES IN MANY-ELECTRON ATOMS

The nature of the solution for normal helium suggests that the energy of other configurations in many-electron atoms may also be expressed in terms of (a) an ideal H-like or He-like term or terms, the He-like term of the form shown in (1) applying with coupled electrons, plus (b) a term or terms due to "adiabatic" orbital distortion for electrons not undergoing radiation in reaching the state. In considering excited ¹S states of two-electron atoms the ideal term should be an H-like term with effective atomic number $Z'=Z-1$, i.e., with perfect screening. We shall designate it H_{*n*} for the state of quantum number n . Now let us postulate on the basis of classical models that the average distortion of the orbit in excited states is proportional to the orbital frequency which seems to be a logical assumption. This suggests also that since the ground state is really a ¹S state, the orbital distortion or resonance term should be proportional to $(Z-k)Rhc/4$, although it is apparent that there is an abrupt change in the characteristics of the orbit due to breaking of the electron coupling. Let us suppose for the moment, however, that this merely introduces a constant factor. Since the frequency factor should be given to a close approximation at least by E_n/nE_1 , where E_n is the term value taken as positive by convention and E_1 is the ionization potential, the following equation should hold according to our postulates for the ¹S

TABLE II. Term values of ¹S series in He and Li⁺ (ev).

State	He		Li ⁺	
	calc.	obs.	calc.	obs.
2's	3.94	3.95	14.74	14.80
3's	1.66	1.66	6.35	6.33
4's	.91	.91	3.53	3.51

TABLE III. Term values of various He-like series from Eq. (4) (ev).

Term	He		Li ⁺		Be ²⁺		B ³⁺		C ⁴⁺	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
2' <i>p</i>	(3.35)	3.35	13.34	13.36	30.06	30.07	53.54	53.53	(83.79)	83.79
3' <i>p</i>	1.49	1.49	5.96	5.96	13.42	13.43	23.89	23.95	37.37	37.39
4' <i>p</i>	.84	.84	3.36	3.36	7.57	7.57	13.46	13.47	21.05	21.06
		(k ₁ = -.52; k = 1.705)								
2 ³ <i>s</i>	(4.74)	4.74	(16.53)	16.53						
3 ³ <i>s</i>	1.86	1.86	6.84	6.82						
4 ³ <i>s</i>	.99	.99	3.72	3.71						
		(k ₁ = 3.92; k = .94)								
2 ³ <i>p</i>	(3.61)	3.61	(14.29)	14.29						
3 ³ <i>p</i>	1.57	1.57	6.24	6.24						
4 ³ <i>p</i>	.88	.88	3.48	3.48						
		(k ₁ = 1.44; k = 1.36)								

TABLE IV. Ground and excited states in Li and Li-like atoms (ev).

	Li		Be ⁺		B ²⁺		C ³⁺		N ⁴⁺		O ⁵⁺		F ⁶⁺	
	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	obs.
2 ² <i>s</i>	(5.36)	5.36	18.03	18.12	37.63	37.74	64.13	64.17	97.33	97.40	137.42	137.43	(184.26)	184.26
3 ² <i>s</i>	2.00	2.01	7.21	7.24	15.50	15.51	26.84	26.81	41.18	41.13	58.56	58.64	78.95	78.84
4 ² <i>s</i>	1.04	1.05	3.87	3.88	8.41	8.42	14.67	14.66	22.63	22.60	32.29	32.29		
							(k ₁ = 6.94; k = 1.724)							
2 ² <i>p</i>	(3.53)	3.53	14.21	14.18	31.80	31.78	56.23	56.22	87.46	87.47	125.50	125.54	(170.30)	170.30
3 ² <i>p</i>	1.55	1.55	6.22	6.22	13.93	13.94	24.68	24.69	38.46	38.46	55.22	55.25	75.02	75.07
4 ² <i>s</i>	.87	.87	3.47	3.47	7.78	7.78	13.79	13.80	21.51	21.50	30.91	30.92	42.01	42.02

states of two-electron atoms:

$$E_n = H_n + k_1(Z - k)Rhc/4 \cdot E_n/nE_1. \quad (4)$$

If we employ values of E_1 obtained from (3) by subtracting one-electron atom ionization potentials, $k = .725$ as in Table I, and evaluate k_1 from the 2'*s* term in helium, values of E_n are obtained which agree with observation within $\pm .01$ ev in He and $\pm .04$ ev in Li⁺. Other experimental data are not available.

In order to investigate the nature of k_1 let us develop (3) in the same form as (4) by rearrangement and subtraction of one-electron ionization potentials. This gives

$$E_1 = H_1 + [(4Z - 3.5)/(Z - k) - 1](Z - k)Rhc/4. \quad (5)$$

Here $((4Z - 3.5)/(Z - k) - 1)$ takes the place of k_1 in (4), but as noted above it differs from k_1 by the effect of electron coupling. It is interesting that this factor while not a constant shows large deviation only in H⁻ and approaches the value 3.0 for large values of Z . Now in normal He the energy assigned to a given electron should be 39.3 ev rather than 24.47 and 54.14 ev, since both the electrons are assumed to be identical. Hence, to be strictly comparable to (4), Eq. (5) for He would apparently contain the frequency factor

39.3/24.47 which if factored from the coefficient of the resonance term would leave 1.585 which agrees closely with the value of k_1 obtained from the 2'*s* state of He. Similarly in Li⁺ the factor 98.55/75.3 · $Z'Z_0/Z$, where Z_0 is the atomic number of the first member of the sequence (2 in this case), when used as the frequency factor in (4) requires the value $k_1 = 1.576$ to agree with (5). Data for excited ¹S states in He and Li⁺ calculated from (4) using $k_1 = 1.58$ are shown in Table II. The significance of the factor $Z'Z_0/Z$ which is unity for the first member of a sequence is shown below.

It is of interest to test (4) in various other series of He-like atoms. Table III lists calculated and observed data for the next three series. The values of the constants k_1 and k which are given in the table were obtained from the term values shown in parentheses. The agreement appears to verify that the form of (4) is essentially correct.

It is not readily apparent what values of E_1 should be used in series of three-electron atoms, if indeed such methods as those used in He are applicable in three-electron atoms. However, we may define H_n by taking Z' equal to Z minus the number of electrons in the atom core. Also we find that the factor $1/n^3 \cdot E_n/H_n \cdot Z'/Z$ is only slightly different from the frequency factor used

in (4). In fact, it would be almost identical if a small constant were subtracted from Z . This factor amounts simply to expressing the ionization constants of He-like atoms by $Z'ZRhc$ where the product $(Z'Z)$ is the square of an effective atomic number. Although $Z'(Z-.2)$ gives closer agreement, for use in the relative frequency factor we may neglect the small constant in Z and adjust the constants of (4) to correct for the error introduced, thus eliminating the necessity of introducing a third constant in (4). We thus have

$$E_n = H_n + k_1(Z-k)Rhc/4 \cdot 1/n^3 \cdot E_n/H_n \cdot Z'/Z, \quad (6)$$

which we shall use to express the term values of the various series in lithium and like atoms. Equation (6) holds as well in He and like series as (4) if the constants shown in Tables II and III are replaced by the following values: 1S : $k_1=1.8$; $k=.725$; 1P : $k_1=-.54$, $k=1.695$; 3S : $k_1=4.14$, $k=.895$; 3P : $k_1=1.53$, $k=1.35$. Table IV gives a comparison of data calculated from (6) and observed data for the 2S and 2P series of Li and Li-like atoms. As before, k_1 and k were evaluated from two experimental points in each series. The general agreement indicates that the empirical frequency factor is essentially correct, and shows that the methods used in two-electron atoms are valid in three-electron atoms as well.

To illustrate by a second example the state of affairs with coupled electrons, we note that the ground states of Be and Be-like atoms are given within $\pm .1$ ev by the equation

$$E = [(4(Z')-1)^2 + 6.94(Z-1.724)E/H_n \cdot Z'/Z - .84(Z-4.0)]Rhc/32. \quad (7)$$

The first term in (7) will be recognized as the

ideal He term for $n=2$ and $Z'=Z-2$. The second term is the resonance term for interaction of the two $2s$ (coupled) electrons with the two $1s$ (coupled) electrons. This term was simply taken over from the three-electron ground states, the effect of the interaction of two instead of one $2s$ electron being accounted for in E/H_n . The last term evaluated empirically accounts for the interaction of the two $2s$ electrons with each other. Note that the ionization potentials of the Be sequence are obtained from (7) by subtracting the corresponding ionization potentials of the lithium sequence.

DISCUSSION

It is of significance irrespective of the nature of the wave characteristics of matter that one can set up simple relations based on classical models for expressing the electronic energies, thus lending additional support to the belief that the Rutherford-Bohr models when properly understood are valid in atomic and molecular structure. That the deviations in many electron atoms from the ideal Bohr structure may be expressed by a term which is proportional to the orbital frequency as determined by classical models seems quite evident from the results of this study. That is, the agreement obtained for higher quantum states than that from which the constants were evaluated is independent of any advantage which may have been gained by the use of empirical constants. Finally, one will discover that the methods used in two, three, and the ground states of four-electron atoms are not limited to these special cases although, naturally, complications must arise as the number of orbital interactions increase.