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NEW ATOMIC STRUCTURE THEORY AND BEAM-FOIL SPECTROSCOPY

Oktay Sinanoglu

Yale University, New Haven, Connecticut

and

Orta-Dogu Teknik Üniversitesi

Ankara, Türkiye

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In the 1960's atomic structure theory entered a new phase. Previous theory had been based on the central field approximation-orbitals in a central field. The central field theory was developed remarkably fast and in a complete way in the 1930's, with efforts that culminated in the classic book by Condon and Shortley. These developments included the formulation of the energy levels in terms of angular momentum coupling coefficients and the radial integrals, the F and G parameters, the comparison of the thus predicted ratios of term splittings with experiment, and the use of simple expressions of various transitions probabilities based on angular momentum theory and reduction to a one-electron integral like $< 2s \mid r \mid 2p >$. Some of these methods were reformulated later using more group theoretical language by Racah.

Basically, all of these important developments, which we may refer to as "traditional atomic structure theory", are based on the orbital picture or approximations to the best orbitals in a system with the self-consistent field as given by the Hartree-Fock (HF) method. Occasionally in this type of theory it has been necessary to include one or two additional configurations, in working with what we may call a first-order configuration calculation, to explain some anomalies in the low-lying energy levels.

In the 1950's it became possible to implement the HF approximation for many atomic states in a totally non-empirical way. In such calculations two methods have been used: 1) the numerical solution of the HF integral-differential equations (which was done originally in the 1930's by the Hartree's), and 2) the expression of the HF orbitals in terms of a finite number of simple Slater orbitals (STO's) as in the following equation:

$$\varphi_i(r_i) = \sum_a c_i^a \chi_i$$

where the c_i^a coefficients and the variable exponents of the Slater orbitals are determined by matrix diagonalization and iteration with respect to the exponents. (In the literature this has been sometimes referred to as "analytic HF").

The numerical methods involved in this technique, which were outlined in the book by Hartree, published in 1957, culminated in the numerical HF programs of Froese-Fischer, which have now been used by many workers to obtain HF orbitals, even for quite heavy atoms. In the analytical method, which was implemented mainly by Roothaan, one needs about six Slater orbitals (STO), for each actual HF orbital. In the first and second-row atoms, with this many Slater orbitals, one obtains results comparable to the numerical HF method. The advantage of the analytic method, is that one needs only a few numbers to specify an orbital completely, rather than a long numerical table for each orbital wave function. However, more recently it has been found that for larger atoms it is considerably more efficient and economical to make the numerical calculation rather than the analytic one.

In the older days of the orbital theory, that is the central field method, or the *F* and *G* method, it seemed that such orbitals could be calculated variationally from one state, and then the same orbitals could be used to calculate another state. For example one could have taken the $1s$, $2s$ or $2p$ orbitals from a HF calculation on $(1s^2\ 2s^2\ 2p^4)\ {}^3P$ of Oxygen, and then use the same orbitals to calculate the expectation value of the same configuration ${}^1S$ state. In more recent times it was found, however that this transfer of orbitals leads to a half e. v. kind of error if the transfer is between different states of the same atom with the same number of electrons and atomic number, and that it leads to errors of several electron volts, if the transfer is made for the same atomic number to different number of electron ions. So, it was concluded that it is necessary to calculate HF orbitals by making a separate HF calculation for each state. Therefore although for example 1*s*, 2*s*, 2*p* are nominally the same, the individual orbitals are different for different states of the same configuration. This means that, for example although the 1*s*, 2*s* orbitals in the ^3P ground state configuration are orthogonal to one another, the 1*s* of ^3P is not orthogonal to the 2*s* of the ^1S same configuration. Therefore, in the calculation of the transition probabilities, for example, the many-electron matrix elements no longer reduce to the product of some coefficient times a given one-electron matrix element, but larger calculations are necessary.

TABLE I

Importance of Electron Correlation in Atomic Properties

	Hartree-Fock	(H. F. + Correlation)	Experiment
Electron Affinity of Oxygen (e. v.)	- 0.54	1.24	1.465
$(SD)/(DP)$ term Splitting Ratio of $1s^2\ 2p^2\ (Z=8)$	1.47	3.66	3.15
Multiplet Oscillator Strength $1s^2\ 2s^2\ 2p^2\ (^3P)$ to $1s^2\ 2s\ 2p^3\ (^3D)\ (Z=7)$	0.236	0.100	0.101 (±0.006)
Binding Energy of F_2 Molecule (e. v.)	- 1.37	-	1.68

Although it would seem that to make HF calculations anew for each new state would be a very difficult undertaking, and that a theory based on such HF wave functions might be very complicated, in practice these difficulties have not caused much hindrance. At present, HF calculations of this type and based on non-closed shell theory are either available in various tables in the literature or there are HF programs which are widely distributed and can be used with ease to obtain the states of interest.

When such HF calculations became available and were accurate enough, it was possible to test the HF central field method for many atomic properties. It turned out, however, that many quantities of interest are not given well enough, as it is shown in Table I. For example, HF is unable to give electron affinity, even where a stable negative ion exists. Furthermore it gives many of the allowed transition probabilities only to within a factor of two or so. Clearly, HF calculations are not adequate to obtain quantitative results. The question then arises whether one must abandon the orbital, i.e. the HF approach and have a completely different theory. There are other things that have to be added to the HF method to get a complete theory. The nature of the HF approximation was physically better understood in the 1960's and it was realized that, although this method is not adequate to give final results, it is an important and perhaps even an essential starting point for the construction of a more complete theory

NEW AGE OF ATOMIC STRUCTURE THEORY

In the modern theory, we shall distinguish between 3 phases of the problem:

1.- Hartree–Fock Theory
2.- Electron correlation
3.- Relativistic Part.

We described the HF aspects above. Starting with a non-relativistic Hamiltonian, electron correlation is defined as the rest of the energy and of the wave function beyond the HF approximation as in eq. 1,

$$E_{NR} = E_{HF} + E_{CORR}. \tag{1}$$

In defining the rest of the wave function (w. f.) one has to use what is called a "correlation normalization" of the wave function. The exact w. f is written as a sum of two parts which are orthogonal to each other,

$$\Psi = \phi_{HF} + \chi \tag{2}$$

with $\langle \Psi | \Psi \rangle = 1 + \langle \chi | \chi \rangle$ and $\langle \phi_{HF} | \chi \rangle = 0$. (3)

Furthermore we have the useful rule that the deviation of the normalization from unity, which is a correlation probability, is roughly the ratio of the correlation energy to the HF energy to the HF energy:

$$\frac{\langle \chi | \chi \rangle}{1} \approx \frac{E_{CORR}}{E_{HF}} \tag{4}$$

For the lighter atoms, as C, O, Al, Ar, one adds a relativistic correction to the energy given by eq. 1. This is usually based on a perturbative treatment of the relativistic changes on the Hamiltonian. However, it has been known, since about 1959, that already in the first two-rows of the atoms the magnitude of this relativistic energy correction can be of the order of the correlation energy itself. Thus, for the first two rows of atoms, and beyond, this usually accepted way of decomposing the total energy is not adequate, and one would expect that the correlation and relativistic effects would affect one another. Thus, we have suggested that the problem be broken up, for the heavier atoms, as: the relativistic HF approximation plus relativistic correlations as in the following equation,

$$E = E_{RELHF} + E_{RELCOR} \tag{5}$$

Of course, since the exact Hamiltonian for the relativistic N-electron case is not known, this has to be based on an approximate Hamiltonian,

$$H_{REL} \cong \sum_{i}^{N} h_{i}^{D} + \sum_{i>j}^{N} g_{ij}^{B} \tag{6}$$

where one assumes a sum of one-electron Dirac Hamiltonians (the Hydrogen atom - like ones) plus two-electron Breit interactions.

Presently, in several centers in the world (Mayers, Weber, Coulthard, and Grant) relativistic HF wave functions are being obtained, based on eq. 6, although this task is much more difficult than in the non-relativistic problem.

Given eq. 6, the electron correlation solution, which we shall outline below, developed for the non-relativistic case, would follow in a parallel way for this relativistic approximate Hamiltonian. While the formal aspects are very similar, it might of course be quite difficult to get accurate, actual results in this case, but no attempts in this direction have yet been made.

Even with this restatement of the problem, there are still many open questions. As, for example, how big do the radiative corrections become for larger atoms and how should they be included.

For the lighter atoms, it is essentially assumed (compare eqs. 1 and 5) that

$$E_{RELHF} \cong E_{HF} + E_{REL} \tag{7}$$

and

$$E_{RELCOR} \cong E_{CORR} \tag{8}.$$

The more relativistic theory for the heavy atoms is still in the future and now that, as discussed below, the non-relativistic correlation problem, both for the ground and the excited states, has been worked out and applied, one may expect that atomic structure theory may go forth in the 1970's in this direction.

The non-relativistic N-electron atom problem, the electron correlation theory, was essentially understood in its basic physical and mathematical features, first for ground states and then for the more complicated excited states, in the period from 1959 to 1969. For details of these developments and other results provided by the new atomic structure theory, which can be applied for more quantitative results in various applications, we refer to some of the key references in the bibliography. Here we shall give a very brief summary of the essential features.

For ground states, more strictly for closed shells, one obtains, by what the author has called the method of successive partial orthogonalizations, the form of the exact wave function Ψ. Here we have 1, 2, 3 up to N-particle correlations separated from one another in a rigorous manner, with the closed form correlation functions obeying orbital orthogonality relations, which come out rigorously from this relation as given in eq. (9).

$$< u_{ij} | k > = 0 . \tag{9}$$

These orbital orthogonality relations turn out to have important physical consequences in the variation of correlation energy with number of electrons and atomic number. One starts with the exact form and then uses "sub-variational principles" (introduced by the author), by which from the different parts of this exact wave function and the corresponding energy expression, different approximate theories can be derived.

In the ground state theory the author found by mathematical and physical arguments that E_{CORR} is given primarily by a sum of all possible "pair correlations" between HF spin-orbitals

$$E_{CORR} < \sum_{i>j}^{N} \tilde{\epsilon}'_{ij} + R' \tag{10}$$

where eq. (10) defines the decoupled pair correlations $\tilde{\epsilon}'_{ij}$ and R' are three and more electron correlation remainders. Each $\tilde{\epsilon}'_{ij}$ is obtained by minimizing these "Helium-like" $2\text{-}e^-$ equations since it is shown that

$$\epsilon_{ij} < \tilde{\epsilon}'_{ij} \tag{11}$$

In the past, quite accurate calculations could be made for the Helium atom with special variational devices, but not for more-electron atoms. With the above theory, it became possible to treat the N-electron atom, by doing several of the new decoupled He-like problem above.

In the meanwhile, two other approaches to electron correlations in atoms have been used by H. Kelly, by Tolmachev, by Cizek, and by K. A. Brueckner and the author. The first is the direct use of the diagrammatic perturbation technique as an algorithm. Kelly was able to implement this by summing (integrating) over an infinite one-electron basis set. Many diagrams were calculated. The important effects, however, turned out to be those predicted by the Sinanoglu many-electron theory (MET). The diagrammatic Kelly algorithms can also be used to evaluate some of the terms in MET like R' in eq. (10).

The other approach is interesting in showing how the atomic problem differs so greatly from the infinite uniform electron gas. Brueckner and the author treated the atomic electrons as a non-uniform electron gas but found the non-uniformity so strong that the results are divergent.

These three approaches are discussed in a recent book by Sinanoglu and Brueckner which includes also some of the historical reprints in the field since 1934.

The various terms and effects in eqs. (9) - (10) can now be completely tested and studied in otherwise not possible detail, by the exact solutions of a model of N-electron atoms–the pseudo–atom of Moshinsky, Novaro and coworkers. This type of study should shed considerable light on the correlation effects of the more complicated types.

EXCITED STATES

Although for ground states, correlations were studied by three approaches (and those derived from these three), for excited states the correlation problem was essentially solved between 1965- 1969 by the "Non-closed Shell many-electron theory" of the author and coworkers. The results turned out to be remarkably simple. Now the HF is the Roothaan non-closed shell HF theory with

$$\Phi_{RHF} = \sum_{k} c_k \Delta_k \tag{12}$$

with several determinants made up of the "Hartree-Fock sea" spin orbitals. For $1s^h\, 2s^m\, 2p^k$ configurations, for example, the HF sea is

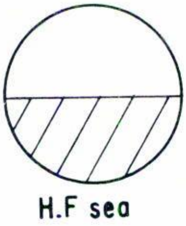
$$\{k\} = \{\, 1s_{\alpha},\, 1s_{\beta},\, 2s_{\alpha}, \ldots,\, 2p_{\beta} \} , \tag{13}$$

a set of *ten* orbitals. From this "sea", the exact wave function of a state (like $1s^2\, 2s^2\, 2p^2\ {}^1S$) is given by

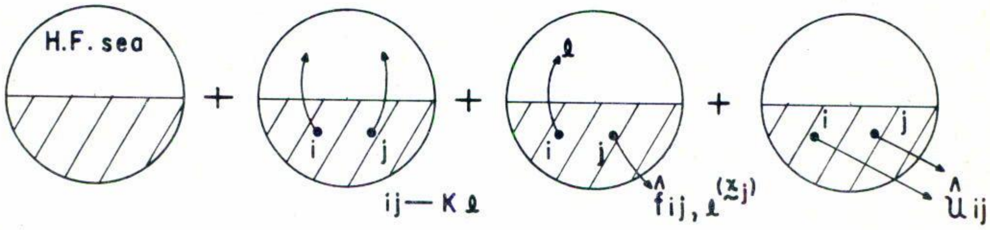
$$\Psi_{EXACT} = \Phi_{RHF} + \chi_{INT} + \chi_F + \chi_U \tag{14}$$

with all parts orthogonal to each other. Here the subindex INT stands for "internal correlation'', F for "semi-internal (plus polarization) correlation", and U for "all-external correlation".

Now we have a partially filled "H-F sea", which includes everything that comes from the finite set of the M spin-orbitals of the HF set:



The total wave function can be displayed as:



(15)

The internal correlation is given by all the determinants within the HF sea (virtual transitions to unoccupied part of sea).

Multi-Configuration SCF is a combination including part of $\Phi_{RHF} + \chi_{INT}$, but it gives only a small improvement in energy for atoms:

$$\Phi_{GRHF} \simeq \frac{\Phi_{RHF} + \chi_{INT}}{[1 + \langle \chi_{INT} | \chi_{INT} \rangle]^{\frac{1}{2}}} , \qquad (16)$$

because $\langle \Phi_{RHF} | \Phi_{RHF} \rangle = 1$. We renormalize if we wish to relate to the Φ_{GRHF} (general restr. HF $\supset$ MCSCF) as the starting point, which is more useful in dissociating-molecule problems.

Now χ_F, the semi-internal part, takes a pair with one e^- going out, the other inside the sea. But now, for the function "outside" where the j orbital goes, depends on where the e^- went. So

$$\mathrm{i} \rightarrow l \quad j \rightarrow \hat{f}_{il,j}(\chi_j),$$

and $\hat{f}$ is orthogonal to the sea orbitals,

$$<\hat{f}_{ij,\,l}|k> = 0 \quad k \in \{1, 2, \ldots, M\}$$

The semi-internal correlation effect seems to have been missed previously in atomic theory. It turned out, when first calculated by B. Skutnik and the author, to be an important effect comparable in magnitude to the other two correlation effects we have discussed.

For all-external correlations, the pair terms are again dominant, just like in the closed shell MET theory. As Wigner noted, excited-state correlations looked very complicated, and there seemed to be no systematics. But now we know that this individualistic behavior comes from χ_{INT} and χ_F. We can calculate them and be left only with closed-shell type χ_U with transferable pairs. All three terms are equally important and should be included in the energy calculations.

In χ_F another term, which we shall call "orbital-polarization" exists and which for closed shells was almost negligible. Here it is important and it is related to $\hat{f}_{ij,\,l}$ by symmetry, so it must be included in χ_F.

The exact energy is then given by

$$E = E_{RHF} + E_{INT} + E_F + E_U \ , \tag{17}$$

but we must resort again to the subvariational principle to get the non-closed shell energy. We get stationary solutions (although we do not necessarily have an upper bound now) for each correlation part using our "subvariational" method. We calculate the first three terms in (17), E_U being given as for closed-shells.

We take the "charge density wave function" as

$$\Psi_{CD} \equiv \Phi_{RHF} + \chi_{INT} + \chi_F \ , \tag{18}$$

since the χ_U does not change the charge distributions very much. For example, for transition probabilities Ψ_{CD} is enough. To calculate the energy we need to include E_U also. We have the HF sea orbitals (including those in the χ_{INT} part) $1s_\alpha \ldots\ 2p_\beta$ plus "semi-internal orbitals" $\hat{f}_{ij,\,k}$. The semiint orbital could come from the integro-differential equations that have been derived, but we must remember that Φ_{RHF} are basis for $SU(2) \otimes O(3)$, but the $\hat{f}_{ij,\,l}$ are not, so we must expand them, as follows

$$\hat{f}_{ij,\,l}(\mathbf{x}_i) = \Sigma\, \hat{f}_L(r)\, Y_{LM}(\Omega)\, \sigma_i \,.$$

This looks as if we had an infinite expansion, but this is not so, because if Φ_{RHF} has a certain symmetry (for example ^1S), χ_F has the same ^1S symmetry. Therefore, in $\mathcal{Q}(1, 2 \ldots l, \hat{f}_{ij,\,l} \ldots u_k)$ the expansion of $\hat{f}_{ij,\,l}$ gives only a finite number of terms in the expansion. For the *KL* sea, for example we have only $L = 0, 1, 2, 3$ and $f_s(r)$, $f_p(r)$, $f_d(r)$ and $f_f(r)$. There would be a set of such radial functions for each ij, l, but there are not many possible combinations. So usually only one set exists in the *KL*-shells because of symmetry. These we shall call "semi-internal orbitals".

We now use a combination of Slater orbitals and use the variational method to determine $f(r)$, i. e., an expansion in STO. Correlation is a second order effect and hence not very sensitive to the "sea-orbitals". For instance, take a single 3^*l STO, but with a variational exponent; this will come out very different from the real $3l$ exponent.

We can now even go to the *M*-shell using the largest computers. Programs developed first by O. Sinanoglu and I. Öksüz, have now been extended to heavier atoms (beyond sodium) by D. Beck. Starting from the HF sea and information with respect to the state number of electrons, etc., the fully automatic program gets the χ_{INT} plus the χ_F terms. First it finds all the internal and semi-internal determinants. It uses the Condon & Shortley methods, spin properties, diagonalizes a matrix and gets coefficients, and then iterates. Only about three iterations are needed in general.

With these methods, one has thus obtained the

$$\Psi_{CD} = \Phi_{RHF} + \chi_{INT} + \chi_F \tag{20}$$

wave functions of hundred of atomic and ionic states.

For energetics, one still needed E_U. But since now the "all-external correlation" E_U is just the closed-shell-like part, it is given by a combination of the previous pair correlations multiplied by group-theoretic pair occupation probabilities, determined by the c_p of Φ_{RHF}. There are only ***eleven*** distinct "irreducible (w. r. t. the $O(3) \otimes SU(2)$ group) pair correlation" energies in the *KL*-atoms. Further theory tells us that these values

TABLE II

Electron Affinities and Excitation Energies of Negative Ion Excited States

		New Atomic Structure Theory (Sinanoglu and coworkers)	"Experimental"
C^-	*E. A.*	1.17 ev.	1.25 ev.
	^2D	1.30	1.29
	^2P	1.99	1.46
N^-	*E. A.*	− 0.45	(?)
	^1D	1.04	1.28
	^1S	2.36	2.60
O^-	*E. A.*	1.24	1.465
F^-	*E. A.*	3.23	3.448

Excitation energies are reported relative to the ground state negative ion.

TABLE III

(SD)/(DP) TERM SPLITTING RATIOS

		New Atomic Structure Theory (Sinanoglu and coworkers)	Observed	Layzer	Bach–Gouds	F G Method
$1s^2 2s 2p^2$	$Z = 6$	2.75	2.30	1.45	4.34	1.50
	$Z = 7$	2.37	2.09	1.46	3.41	1.50
	$Z = 8$	2.12	1.92	1.47	3.07	1.50
$1s^2 2p^2$	$Z = 7$	4.44	3.49	2.03	–	1.50
	$Z = 8$	3.66	3.15	2.03	–	1.50

are ***transferable*** from state to state, ion to ion. Thus, they can be evaluated from a few states and then used to predict the other E_U to a deviation like ± 0.02 ev.

Thus, from $E_{RHF} + E_{INT+F}$ and now the E_U, one simply gets the energies of various atomic ions or states. These yield now good term splitting ratios, excitation energies, electron affinities, etc., compared to experiment. Traditional methods were often even qualitatively wrong for these properties (cf. Table I).

In Tables II and III, we show sample comparisons of traditional methods with the modern theory on energy type atomic properties.

TRANSITION PROBABILITIES

We saw also in Table I that, the orbital methods give the important $E1$ electric dipole allowed transition probabilities to usually no better than a factor of two.

Transition probabilities are important in astrophysics and in atmospheric physics. One must also know how to calculate them in atoms before hoping to get them for molecules. Study of the aurorae, of chemical abundances of elements in the sun and the stars, stellar dynamics require accurate values of these transition probabilities (A_{mn}).

Earlier experimental methods were based on measurement of light intensity in emission or absorption in high temperature gases in furnaces, arcs, etc., These require a knowledge of the number density of the species involved. Further, one cannot eliminate the competing decay processes due to collisions. Thus, these methods were unreliable and also gave the A_{mn} to no better than a factor of two.

At the same time as new theory began to give accurate A_{mn} in the last few years, new experimental methods also achieved A_{mn}'s accurate to 3–10%. The new methods are mainly the phase shift method and the beam foil spectroscopy invented by Bashkin. The latter is a new powerful tool which opens up new directions in atomic physics.

A beam of atoms is accelerated to a kinetic of 1–5 nev.. The atoms then pass through a thin carbon foil (e. g. 200 Å thick). Past the foil there is a pencil of light of decreasing intensity. The decrease gives the lifetime of atoms excited at the foil. If there is no complication due to cascade processes ($\tau = 1/\Sigma A_{mn}$) τ yields directly an $A_{i \to f}$. Applying an electric field accross the beam, one separates different charge states.

The new atomic structure theory calculates the $E1$ and $E2$ transition probabilities, the multiplet oscillator strengths from the charge distribution affecting part of the wave function

$$\Psi_{CD} = \Phi_{RHF} + \chi_{INT+F} \tag{20}$$

Then many-electron matrix elements with such many determinant wave functions for initial and final states are calculated with computer programs (Westhaus and Sinanoglu). Recall that as mentioned in the first section, now the same name orbitals from two different states are no longer orthonormal, though they were in the "central field" era. Thus, special transformation methods are required and are used as matrix elements no longer reduce to a simple one electron matrix element like $< 2s | r | 2p >$.

Table IV shows a sample of multiplet oscillator strengths (related very simply to $A_{i \to f}$) with the modern theory and the new experiments which we saw have the significant correlation effects complete in both the ground and the excited state (whereas traditional C.I. would keep adding configurations, some of which may belong to χ_U and not contribute much, while missing significant effects like χ_F (semi-internal)).

Forbidden transitions like the electric quadrupole ($E2$) oxygen green line (5577 Å) arising within $1s^2 2s^2 2p\, 4s$, are also calculated as above with the new theory. Here the effect of correlation on HF is less, about 20-30%, though of course it has to be included for accurate values. The theoretical values can now be used e.g. in the study of upper atmosphere electron densities by looking at the aurorae. They were used also to revise abundances of carbon and oxygen in the sun.

Unlike the allowed case, forbidden $A_{i \to f}$'s cannot be measured by beam-foil. As τ is ca. 10^8 times longer, atoms would have to travel in a table 10^8 cm or 1000 kms before showing a decreasing intensity of light! So still two, three recent experimental attempts have been made but these are of the bulk gas type and gave $A_{i \to f}$'s only to about a factor of two. New experimental methods are badly needed for forbidden lines. This is a real challenge for experimentalists.

We have seen above that for lighter atoms (say Boron to Argon) both modern theory and experiment are now quantitative. The beam-foil spectroscopy opens up still another domain of atomic physics:

The High Z, Low N Realm

If the atomic beam is accelerated e.g. with a Tandem linear accelerator to energies over 5.5 nev., one can produce ions of high atomic number Z, but very few electrons N. (Recently Marrus in Berkeley has made experiments with even He-like Bromine!). Such highly positive ions could never be observed in the laboratory before, but only in the sun. The new study of their spectra should be very useful in solar physics. At present many of the lines in the far and x-ray solar spectra (obtained by rockets from above the atmosphere) are unidentified.

Further, accurate knowledge of the highly ionized energy levels is important even in calculating the binding energies of molecules in theoretical chemistry. One needs to know the total energies of the constituent atoms. These are obtained by adding all the ionizational potentials (I.P.). But a look at C. Moore, "Tables of Atomic Energy Levels" shows very few levels and I.P.'s are known in the high Z, low N realm.

We mentioned in Section 1, the relativistic problem. Clearly the third phase of atomic structure theory will have to move in that direction. New relativistic treatments of electron correlation added to relativistic HF, study of radiative corrections, etc., can best be tested on high Z, low N ions. How do transition probabilities behave in this region for example? Much new theory and experiment will be needed in this realm.

Some Other Related Problems

The methods introduced in the last decade for the treatment of ground and excited state atoms, are methods more generally for N-fermion systems. Can they be applied to finite nuclei? It appeared at first that they could not be, at least not without much too drastic modifications. This was due to the "hard-core" in the nucleon-nucleon interaction, g_{ij}^{nn} . With a hard-core, which the earlier potentials had already, the ordinary HF method gives infinities. So progress in that field was mainly on infinite nuclear matter, with results attempted to be taken over into finite nuclei through local nucleon densities, as in the Thomas-Fermi model. But we know in atoms, for example, infinite electron gas problem is very different due to the geometry from the atomic problem. I mean the finite spacing between the orbital levels in the latter. Thus finite nuclei too remained a problem.

However, some nuclear physicists (like A. Kerman, who lectured at the 1971 Latin American School of Physics) believe one does not need the hard core in the two-nucleon potential. They think the scattering data, etc.

can be explained by a "soft" local potential added to a "soft" non-local potential. If so, then all our new N-electron theory would apply to finite nuclei. One has then, a finite ordinary Hartree-Fock method. Therefore, all the rest of the problem is also finite. Of course now the technical aspects are more complicated, we have a tensor force, etc. Also, the relative importance of say $n > 3$-correlations compared to true (decoupled) nucleon pair correlations will no doubt be difficult. Perhaps one can not even have decoupled pairs as in MET, so that one would have to derive higher coupled approximations which however could be explored conveniently using our "subvariational principle" combined with the Hilbert space finite decomposition tool we have.

Finally there is the whole fields of molecular electronic structure and potential energy surfaces for reactive scattering. The MET, N-electron theory applies to these problems. In fact, we already know that the binding energy w.r.t. atoms of a molecule, given by

$$B.E. = E_{MOLEC} - E_{ATOMS} = \Delta E_{HF} + \Delta E_{CORR}$$

i.e. "Hartree-Fock binding" plus "correlation binding", gets a large contribution, sometimes all, from ΔE_{CORR}. Previously in so called "quantum chemistry", chemical binding was always described in terms of some orbital picture. These are basically approximations to or similar to (even valence bond) the HF (Molecular Orbital) method. Recent calculations show that binding energy of a molecule like F_2 gets a large contribution from the newly found "semi-internal correlation". Some semi-empirical methods for ΔE_U have also been developed (Pamuk, Hollister, Sinanoglu, 1966, 1969).

Nevertheless, very little is known quantitatively in this new phase of molecular electronic structure theory. For potential energy surfaces, things are even more at a beginning stage.

Thus many problems remain as challenges for the physicist in the "low energy" domain.

TABLE IV

SPECIES	TRANSITIONS	λ(Å)	f (RHF)	f (Z) (footnote g)	f (NBS)	f (MET)	f (EXP)
CII	$1s^2\,2s^2\,2p\;{}^2P \rightarrow 1s^2\,2s2p^2\;{}^2D$	1335	0.263	0.204	0.17^{a1} $(0.121)^{a2}$	0.125	0.114 $(\pm.011)^b$
NII	$1s^2\,2s^2\,2p^2\;{}^3P \rightarrow 1s^2\,2s2p^3\;{}^3D$	1085	0.236	0.192	0.17^c	0.100	0.109 $(\pm.011)^b$ 0.101 $(\pm.006)^d$
NII	$1s^2\,2s^2\,2p^2\;{}^3P \rightarrow 1s^2\,2s2p^3\;{}^3P$	916	0.170	0.213	0.22^c	0.137	0.131 $(\pm.007)^d$
NII	$1s^2\,2s^2\,2p^2\;{}^3P \rightarrow 1s^2\,2s2p^3\;{}^3S$	645	0.334	0.244	0.23^c	0.218	0.189 $(\pm.016)^d$
NIII	$1s^2\,2s^2 2p\;{}^2P \rightarrow 1s^2\,2s2p^2\;{}^2D$	991	0.213	0.167	0.18^e	0.114	0.103 $(\pm.010)^d$
NIII	$1s^2\,2s^2 2p\;{}^2P \rightarrow 1s^2\,2s2p^2\;{}^2P$	686	0.577	0.415	0.45^e	0.399	0.416 $(\pm.075)^d$
OIII	$1s^2\,2s^2 2p^2\;{}^3P \rightarrow 1s^2\,2s2p^3\;{}^3D$	834	0.200	0.162	0.15^c	0.100	0.102 $(\pm.002)^f$
OIII	$1s^2\,2s^2\,2p^2\;{}^1D \rightarrow 1s^2\,2s2p^3\;{}^1D$	600	0.534		0.37^c	0.297	- -
OIV	$1s^2\,2s^2\,2p\;{}^2P \rightarrow 1s^2\,2s2p^2\;{}^2D$	789	0.179	0.141	0.15^e	0.106	0.091 $(\pm.002)^f$

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