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Ionization Radii of Compressed Atoms

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The compression of all atoms has been modelled by changing the free-atom boundary condition obeyed by electronic wavefunctions, from $r \xrightarrow{\text{lim}} \infty$, $\Psi(r) = 0$ to $r \xrightarrow{\text{lim}} r_0$, $\Psi(r) = 0$, $r_0 < \infty$, in numerical Hartree–Fock–Slater calculations of electronic energy levels. As r_0 decreases, energy levels increase uniformly and by transferring the excess energy, an electron escapes from the valence shell when compression reaches a critical value of r_0 , characteristic of each atom. These ionization radii display remarkable periodicity, commensurate with the known chemistry of the elements, and introduce a new fundamental theoretical parameter that could serve to quantify chemical reactivity. Insofar as the compression of atomic wavefunctions occurs within crowded environments that lead to chemical interactions, ionization radii provide a more realistic index of the chemical properties of atoms in the bulk, than ionization energies, which are more appropriate in spectroscopic analyses of free atoms.

The problem of a compressed hydrogen atom has been considered by several independent authors over a period of many years,^{1–5} with a view to providing a theoretical framework to analyse the spectroscopic and chemical behaviour of atoms under applied pressure. Many other atomic properties, such as electron density in condensed phases and chemical reactivity, are formally related to the same question, but the suitability of hydrogen with its solitary electron, as a representative model in these situations, is debatable. Extending the treatment to non-hydrogen atoms requires a numerical approach and is the topic of this study.

The normal hydrogen problem, in summary, requires solution of the Schrödinger equation, $H\Psi = E\Psi$, under the assumption that the total wavefunction is a product of radial and angular parts,

$$\Psi(r, \theta, \phi) = \frac{1}{r} P(nl; r) Y(\theta, \phi)$$

which allows separation of the variables. Y is a spherical harmonic for integer $n > l \geq 0$, with $n - l - 1$ nodes at $r > 0$. The radial function is a solution of

$$\left[\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} - \frac{1}{n^2} \right] P(nl, r) = 0$$

in atomic units and the boundary conditions $P(nl, 0) = 0$ and $r \xrightarrow{\text{lim}} \infty$, $P(nl; r) = 0$. For the compressed hydrogen atom the latter is replaced by the artificial boundary condition $r \xrightarrow{\text{lim}} r_0$, $P(nl; r) = 0$, for some $r_0 < \infty$.

This corresponds to an impenetrable potential barrier, spherically surrounding the atom at a radial distance r_0 . The symmetry of the coulomb field and hence the angular-dependent part of the wavefunction is not affected by this condition. Apart from the electron density which obviously changes, the most dramatic effect of such compression is the general increase in all electronic energy levels. Calculations are commonly divided into three regions: (i) the bound region where $E < 0$; (ii) the critical region around $E \approx 0$; and (iii) the ionized state, $E > 0$. The first region provides an insight into the spectroscopic effects of applied pressure and condensed phases, and the ionized state probably relates to chemical activation effects. It corresponds to a particle in a

spherical box and is the simplest to solve. The solutions

$$R_{kl} = j_l(kr)$$

with $(\hbar k)^2 = E/2m$ are spherical Bessel functions. The boundary condition becomes $j_l(kr_0) = 0$, which for j_0 becomes $\sin(kr_0) = 0$, i.e. $kr_0 = n\pi$, $E_{n0} = (\hbar n\pi)^2/2mr_0$ for any integer $n > 0$. The critical point for hydrogen ($E_1 = 0$) occurs at $r_0 = 1.835a_0$.

Non-hydrogen Atoms

The interpretation of experimentally measured electron-density functions in condensed (crystal) phases could obviously benefit from information about actual atomic wavefunctions and energy levels. In the first approximation these would correspond to the wavefunctions and energy levels of spherically compressed atoms. For an N -electron atomic system of Hamiltonian

$$H = -\frac{1}{2} \sum_{i=1}^N \left(\nabla_i^2 + \frac{2Z}{r_i} \right) + \sum_{i>j} \frac{1}{r_{ij}}$$

formal solutions of the Schrödinger problem are not known. The most successful procedure to obtain reasonable solutions for these systems is the Hartree–Fock variational method, based on the central-field approximation. This replaces the exact Hamiltonian by

$$H = \sum_{i=1}^N \left\{ -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + U(r_i) \right\}$$

where $U(r_i)$ is a single-particle potential introduced to approximate the inter-electronic interactions. The equation, $H\phi = E\phi$, is now separable provided ϕ is a product of one-electron functions, $\phi = \phi(1)\phi(2)\dots\phi(i)\dots\phi(N)$, to give

$$\left[-\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + U(r_i) \right] \phi_i = E_i \phi_i$$

for all i , which is the wavefunction for an electron in a central field. More concisely $[-(1/2)\nabla_i^2 + V(r_i)]\phi_i = E_i \phi_i$, where $V(r_i)$ is the sum of the nuclear coulomb potential, the total electronic coulomb potential and the exchange potential. Like the hydrogen equation this also separates into radial, angular and spin parts,

$$\phi(r, \theta, \phi) = \frac{1}{r} P(r) Y_{lm}(\theta, \phi) \mu_s$$

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where Y is a spherical harmonic as before. The radial function, for each electron, is now a solution of

$$\left[-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} + V(r) \right] P_{nl}(r) = E_{nl} P_{nl}(r)$$

with boundary conditions, $P(0) = P(\infty) = 0$. The integer n now orders the solutions so that $n = l + 1$ corresponds to the lowest eigenvalue of an eigenfunction without nodes, and so forth. It assumes the same role as the principal quantum number in the hydrogen problem.

A radial equation like this must be solved for each combination nl (called an orbital) and in each case a different exchange potential must be calculated. This is computationally the most difficult part. The Slater⁶ simplification of this problem replaces the exchange potentials for different orbitals by a universal exchange potential formed by suitable averaging over the individual exchange potentials.

In the program by Herman and Skillman,⁷ chosen for the present study, self-consistency is achieved by defining the total potential as

$$V(r) = -\frac{Z}{r} + \frac{1}{r} \int_0^r 4\pi(r')^2 \rho(r') dr' + \int_r^\infty 4\pi(r') \rho(r') dr' - 3 \left[\frac{3\rho(r)}{8\pi} \right]^{1/3}$$

The spherically averaged charge density is defined in terms of the radial wavefunctions

$$\rho(r) = \frac{1}{4\pi r^2} \sum_{nl} W_{nl} [P_{nl}(r)]^2$$

where W_{nl} is the occupation number of the nl subshell. The last term represents the Slater⁶ free-electron exchange approximation.

In this Hartree-Fock-Slater (HFS) scheme, Ψ is represented by a single determinantal wavefunction built up from spin-orbitals, so that the same radial function is assigned to both spins with the same orbital. Open-shell configurations are treated like those with closed shells only and the multiplet splitting is completely ignored. The free-electron exchange approximation is used only in the interior region to ensure correct asymptotic behaviour far out.

The radial equation is solved in an iterative fashion. A starting energy eigenvalue is guessed and the equation is numerically integrated in two directions. Outward integration by the Noumerov method starts from the origin and meets the inward integration from infinity, using the appropriate boundary condition in both cases. From the mismatch of the inward and outward logarithmic derivatives, a correction for the initial energy eigenvalue is calculated and the procedure continued to convergence. Once all P_{nl} are known, a charge density is calculated and used to form a new potential as input for the next cycle in the self-consistent procedure.

Method of Study

Numeric calculations of electronic wavefunctions and energy levels was done with the standard computer program of Herman and Skillman,⁷ previously only used for free-atom or ion calculations, and modified to operate under the same artificial boundary condition described above for the hydrogen atom. The published⁷ FORTRAN code was used with minor modifications and addition of the option to introduce a spherical barrier at r_0 . This is achieved by multiplying the self-consistent-field wavefunctions before normalization and during each iteration cycle by the step-function

$$S = \exp[-(r/r_0)^p]$$

Table 1 Electronic energy levels of the free and compressed praseodymium atom

level	electrons	energy/Ry	
		free atom	compressed to 5.6 a_0
1s	2	-2933.4	-2933.2
2s	2	-460.82	-460.63
2p	6	-437.33	-431.13
3s	2	-100.12	-99.92
3p	6	-89.740	-89.545
3d	10	-70.247	-70.052
4s	2	-20.046	-19.854
4p	6	-16.093	-15.901
4d	10	-9.0790	-8.8867
5s	2	-2.9108	-2.7231
5p	6	-1.8372	-1.6544
4f	3	-0.8102	-0.6197
6s	2	-0.3417	-0.3011

The sharpness, whereby the function changes from 1 to 0 around r_0 depends on the value chosen for $p \gg 1$, as shown graphically in Fig. 1. The choice is left as an option in the program, which searches automatically, once self-consistency has been reached, for the point at which the longest wavefunction fades to zero. A value of $p = 20$ was used for all the calculations in this study.

Two different strategies were explored to avoid the possibility of excising far-out nodes: moving the barrier in by small steps, or imposing it directly at the final r_0 . The same self-consistent field is invariably found by either approach. Starting parameters for any calculation are conveniently available in the form of the published⁷ free-atom potentials and energies. All these data are now available, together with the program, on computer file to interested users.

As a first test of the modified program, it was used to examine how the energies of occupied levels varied during compression and if the critical region for each atom could be identified from the results. The praseodymium atom, as an example, serves to illustrate most of the principles. On compression to 5.6 a_0 ($r_0 = 5.0$, $p = 20$) the energy levels all shift by an almost uniform amount, as shown in Table 1. Relative to their absolute values, the core levels are seen to be hardly affected. For all levels, 1s to 4s, the shift is less than 1% and only for 4f (24%) and 6s (12%) is it more than 10%. In practice this means that all deep core levels could be ignored when the process of ionization is considered.

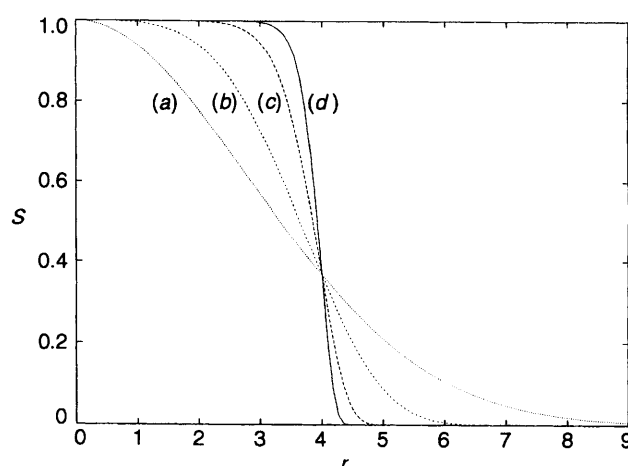


Fig. 1 Step function, $S = \exp[-(r/r_0)^p]$, for values of $p = 2$ (a), 4 (b), 10 (c) and 20 (d) and $r_0 = 4$

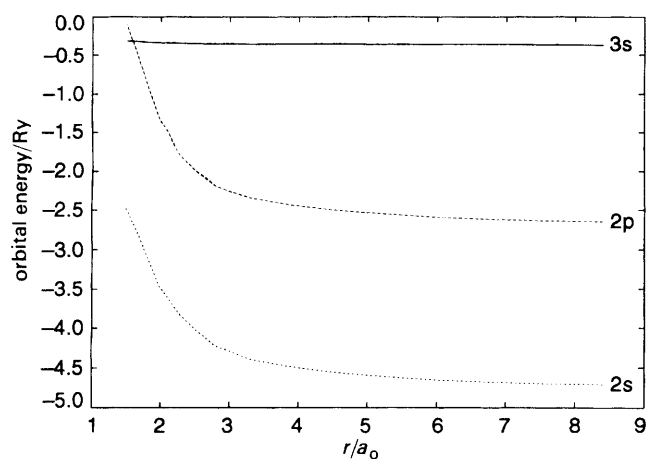


Fig. 2 Orbital compression curves for sodium

As another example, Fig. 2 graphically illustrates the behaviour of the upper levels of the sodium atom under compression. In this case the 3s level is virtually unaffected by compression, but a dramatic increase in the 2p level occurs. Another typical situation is shown in Fig. 3 which represents compression of the vanadium atom, one of the cases where levels cross. This should not be interpreted as an escape of an electron from the 3d level. Each curve represents the centre of gravity of a multiplet of levels and substantial mixing must obviously occur on compression.

This interaction between the levels transfers energy by a process of resonance to a single electron which is pushed to the ionization limit. This process is not unlike ionization in an applied field, often visualized in terms of Fermi's golden rule.⁸ This links the probability of resonance between levels to the density of states in the energy gap. For a separation of ΔE between upper and lower levels, where the latter has an occupation number of N (electrons), the probability is $P = N/\Delta E$, with a maximum of $P = 1$, which describes fully resonating levels. Note that the probability for resonance within the multiplet at the highest level, is likewise equal to unity. The energy transferred from all lower levels to the topmost level is therefore calculated as $E_T = \sum_{i=1}^{n-1} N_i \varepsilon_i / \Delta E_i$, where ε_i is the increase in energy due to compression. Since the N_n electrons at the highest level resonate amongst themselves in the same way, the compression produces an enhancement of the highest one-electron level by an amount $E_p = E_T + N_n \varepsilon_n$, measured from the highest group level.

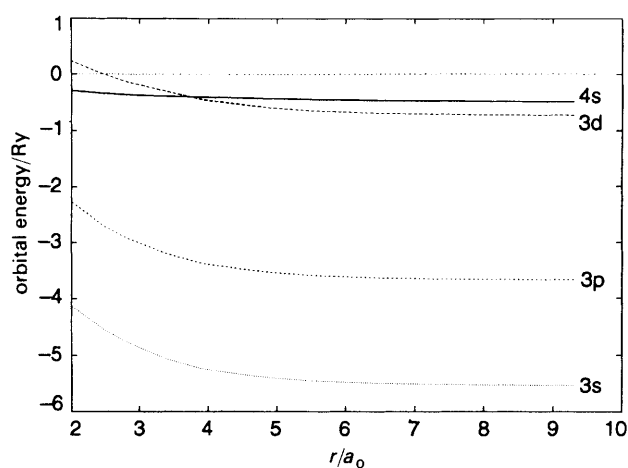


Fig. 3 Orbital compression curves for vanadium

When E_p has increased to match the binding energy of the highest valence level, ionization occurs, and the corresponding value of r_0 represents the ionization radius.

This mechanism is a function of the simplifying assumptions, made to enable integration of the radial equation and is not unique to compressed atoms. A parallel situation exists for a free atom in an ionizing field, V_i . The two systems have the same ground state, i.e. $r_0 = \infty$ or $V_i = 0$. It is only in this state that the quantum numbers n and l are integers.^{1,2} In all other states they are only assumed to be integral and assigned the same ground-state orbital occupation numbers. This raises the energy levels, rather than redistributing electrons to excited levels. Furthermore, for ionization to occur it is necessary for one orbital energy term, $E = (1/n^2)$ to approach zero and thus for an effective quantum number $n \rightarrow \infty$. The implied, infinite number of excited states that feature in this process are never considered in spectroscopic analyses, and transitions are approximated by the FGR procedure. In the present instance it is not the total energy, but only the excess-over-ground-state, or compression shift, that represents excitation and contributes to the one-electron promotion. This means, that the monovalent ion produced in the process has the same ground state (at r_0) as the free atom, except for the loss of one electron. This is the best reason for not moving away from the free-atom orbital structure in the course of the calculation.

This calculation cannot produce ionization energies because the multiplet structure is neglected. Only group potentials can be obtained and these correspond to atomic ionization energies only for singly occupied valence levels.⁹ Alternatively the compression calculation can be repeated for monovalent ions to calculate ionization energies by difference. This has not been done because the ionization radii are considered to provide a more meaningful parameter characteristic of the chemical behaviour of atoms.

Results and Discussion

The program⁷ was finally modified to increase the compression steadily and at each stage to calculate the contribution from all levels to the overall promotion energy. This enables the ionization radius to be determined by a simple graphical procedure, as shown in Fig. 4 for the oxygen atom. By this procedure the ionization radii of all atoms, He–Ha, were determined, using 1985 IUPAC electronic configurations.¹⁰

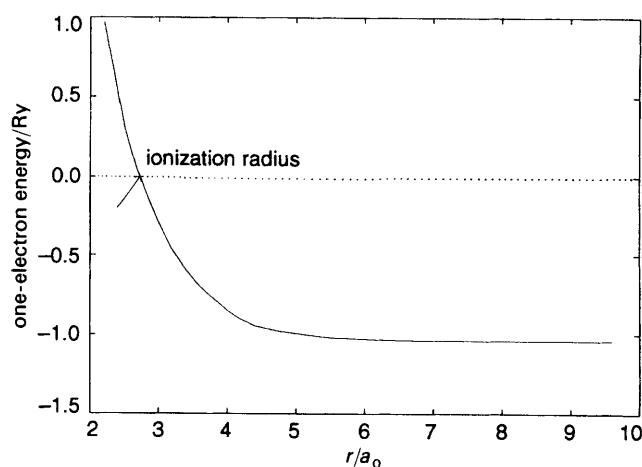


Fig. 4 One-electron compression curve for the valence level of oxygen

[illegible]

state is best described in terms of a valence electron, decoupled from the nucleus, and a monopositive core. The valence electron is confined to the sphere $r \leq r_0$ and described by the spherical Bessel functions that tend to zero at r_0 . The first few of these, as normalized wavefunctions, are

$$\begin{aligned}j_0 &= 0.2251k^{3/2} \sin(kr)/kr \\j_1 &= 0.1928k^{3/2}[\sin(kr) - kr \cos(kr)]/(kr)^2 \\j_2 &= 0.1742k^{3/2}[3 \sin(kr) - kr \cos(kr) - (kr)^2 \sin(kr)]/(kr)^3\end{aligned}$$

The freed (valence) electron is described by a spherically symmetrical state function made up of a normalized linear combination of spherical Bessel functions,

$$\Psi = N \sum_l c_l j_l$$

For states of spherical symmetry the values of c_l depend on the number of spherical harmonics Y_{lm} , viz. $N_l = 2l + 1$ and $c_l \propto (N_l)^{-1/2}$. In chemistry, these are the linear combinations sp^3 , sp^3d^5 , etc. The radial part of these functions is shown in Fig. 6. The range of l , within $0 \leq l \leq 3$, depends on the orbital angular momentum of the valence electron and the

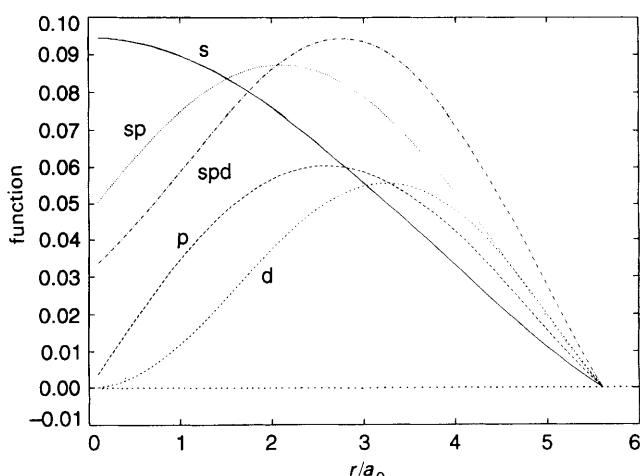


Fig. 6 Linear sums of normalized spherical Bessel functions truncated at $r_0 = 5.6 a_0$

coefficients further depend on the details of the resonance that produces the valence state. The details will therefore differ between atoms, but all valence-state functions will have several features in common. They will be nodeless functions between 0 and r_0 , slowly varying and thus representing states of low kinetic energy.

This explains why the properties of electron-pair bonds could be calculated¹¹ rather well from atomic wavefunctions like $\Psi = (3c/4\pi n)^{1/2}(1/r_0)\exp[-(r/r_0)^p]$. In this expression c is a constant, n is the principal quantum number of the valence electron and r_0 is an empirically established atomic radius. The correspondence between these radii and those newly established here, is almost exact.

It is noted in conclusion that the same procedure can now be developed without resort to any empirical parameters. The ionization radii which describe the response of electronic charge clouds to environmental crowding are calculated from first principles. No other parameters are needed in order to formulate valence-state wavefunctions, and from these, the properties of chemical bonds can be calculated directly.

Further study of the wavefunctions in the critical region around r_0 is now required to establish the correct valence-state functions for each atom. Note how Sommerfeld and Welker² also identified this important region for further

study and showed that it could be approximated by Bessel functions.

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