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RELATIVISTIC PHENOMENA IN ATOMIC AND CHEMICAL PHYSICS: OPPORTUNITIES FOR STUDIES WITH SYNCHROTRON RADIATION*

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Opportunities for investigations in atomic and chemical physics are summarized that may arise as next-generation synchrotron-radiation sources become operational. Recent progress in the study of relativistic effects in atoms is reviewed and some applications to chemistry are discussed. It is pointed out that measurements with highly monochromatic, tunable hard X-rays will make it possible to perform important tests of relativistic phenomena in atoms and molecules.

1. Introduction

The study of atoms and molecules with synchrotron radiation has become an active field [1, 2]. The advent of high-intensity, high-resolution tunable monochromatic beams of vuv and soft X-ray photons with a sharp time structure has made it possible to explore dynamical processes in atomic and molecular photoionization over a wide energy range. Progress is being made in gaining insight into the processes that occur during photoexcitation and escape of the photoelectron through the anisotropic molecular field, in terms of such physical observables as photoionization cross sections and branching ratios, photoelectron angular distributions, and spin polarization of photoelectrons [3]. As pointed out by Dehmer et al [2], particularly important probes in this context are resonant photoionization mechanisms, such as shape resonances and autoionization, in which the excited complex is temporarily trapped in a quasibound state, so that the excited electron traverses the molecular core many times before it escapes by tunneling or by exchange of energy with the core. Resonances thus amplify the subtle dynamics of the electron–core interaction.

Work on *shape resonances* is being extended to other and very different systems than the well-studied N_2 and CO [4, 5] and will include new facets such as vibrational effects in polyatomic molecules, continuum–continuum coupling, and interaction with autoionizing states.

Autoionization in atomic and molecular photoionization still offers much room for productive study [6]. This is well-known to be a multichannel process in which a resonantly excited discrete state from one channel couples to the underlying electronic continua of one or more channels leading to ionization. The requisite high

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*Dedicated to Academician D. Berényi on his 60th birthday.

resolution for synchrotron-radiation studies of autoionization processes is being attained [6] and has led, for example, to triply differential studies of complex autoionization structures in O_2 [7], CO [8] and CO_2 [9], in which the competition between overlapping and autoionizing resonances can be resolved. Sophisticated insight into autoionization phenomena has been achieved for H_2 in terms of multichannel quantum defect theory [2], and extension to other diatomics and more complicated systems can be anticipated.

X-ray emission spectra measured with high resolution can be very useful to elucidate the properties of excited and ionized atoms and molecules [10, 11]. Particulary interesting recent results include electron-beam excited fluorescence of water vapor [12] and CO [13]. Qualitative interpretation of these spectra can be based on CI wave functions built from separately optimized molecular orbitals [12]. What makes the subject particularly interesting and timely is the success, for example by Larkins' group [14], of *ab initio* molecular orbital self-consistent-field calculations of the energy and intensity of X-ray transitions in simple molecules. This work has shown that a realistic basis for comparsion with experiment can be achieved through multi-center relaxed Hartree–Fock calculations. More generally, the analysis and interpretation of *ab initio* molecular wave functions in comparison with measured observables provides a unique and sound basis for determining the importance of various mechanisms.

We can consequently expect growing interest especially in molecular X-ray emission spectra, and clearly the high monochromaticity and tunability of synchrotron radiation makes it an ideal means to excite flourescence. These properties are particularly important because chemical applications of X-ray spectra excited by traditional means have been inhibited by the general occurrence of multivacancy processes. The presence of spectator holes manifests itself in emission spectra by satellite lines, and opening of channels to these initial configurations leads to additional features in absorption spectra [16]. With synchrotron radiation, high-resolution emission spectroscopy can be carried out as a function of exciting photon energy in regions containing both single- and multiple-vacancy thresholds. This technique, already successfully applied in Auger spectroscopy [17, 18], has been demonstrated by Deslattes and coworkers [16] to be eminently suited for the analysis of multi-vacancy effects in X-ray emission spectra and is likely to lead to exceedingly interesting studies, not only of pure single-vacancy molecular X-ray spectra but also of correlation mechanisms that lead to multiple excitation processes.

Polarization of molecular X-ray fluorescence may become an important new technique for the study of molecular systems [19, 20]. Recent experiments on the National Bureau of Standards beam line in the National Synchrotron Light Source have shown high polarization of the X-ray fluorescence following K-shell excitation of several Cl-containing molecules. The Cl $1s$ electrons were resonantly excited, and the subsequent Cl $K\beta$ fluorescence was found to be strongly linearly polarized, with the direction of polarization determined by the symmetry of the valence orbital involved in the fluorescence decay that fills the Cl $1s$ vacancy. For example, in CH_3Cl, valence orbitals of σ symmetry produce fluorescent X rays polarized parallel to the synchrotron-radiation polarization, while fluorescence from π orbitals is polarized perpendicularly to the synchrotron-radiation polarization [19]. In sulfur $1s$ threshold excitation of SF_6, broadened emission features were detected that depend strongly on polarization [21]. These discoveries may lead to the development of a sensitive probe for the study of orbital symmetry in more complicated molecular systems, condensed matter, and adsorbates [19].

A further class of new applications of the next-generation synchrotron-radiation sources, not yet realized, will be based on the possibility of generating light with *continuously variable polarization*, from linear through elliptical to circular [22]. This can become an extremely powerful aid in spectroscopy, particularly for chiral molecules [23].

Synchrotron radiation has opened vast possibilities for the study of *dissociation processes,* occurring either in competition with or subsequent to molecular photoionization. Tunability of the radiation permits preparation of molecular ions with well-defined internal energy, and the sharp time structure of the light permits measurements of threshold photoelectron–photoion coincidences by time-of-flight spectrometry [24]. Astonishingly site-specific fragmentation of small molecules following soft X-ray excitation was demonstrated by Eberhardt and coworkers at NSLS [25]. The same group recently performed coincidence experiments between energy-selected Auger electrons and the ions produced in events following the absorption of a soft X-ray photon by a CO molecule [26]; the results lead to new insight into the potential energy curves of the doubly charged molecular ion and the involvement of individual valence electrons in the molecular bond.

An approach to molecular photoionization and photodissociation dynamics that can be expected to benefit greatly from the next-generation synchrotron-radiation sources, such as Super-ACO in Orsay and the Berkeley ALS, is *multiphoton ionization* photoelectron spectroscopy. In particular, the combination of resonantly enhanced multiphoton ionization with photoelectron spectroscopy is likely to become a very versatile and powerful technique [27]. New kinds of related "two-color" experiments will become possible, in which a laser is used in conjunction with radiation from insertion devices in the new sources [23].

Among the many facets of atomic and molecular physics that are becoming accessible for study with synchrotron radiation, we devote the remainder of this paper to the role of relativistic effects, which have been quite extensively investigated in atomic physics and very likely may offer opportunities for fruitful further insights into molecular structure and dynamics.

2. Relativistic effects

2.1. Nature of relativistic effects in atomic structure and transitions

For the sake of perspective, it is useful to look briefly at the more readily calculable relativistic effects in *atomic structure* and transitions [28]. Relativity notably redistributes the electronic charge in an atom. The relativistic mass increase of fast-moving *s* and *p* electrons close to the nucleus reduces the mean radial distance of these electrons from the origin. A simple hydrogenic calculation [29] shows that the electron-mass increase, and hence, the change in orbital radius, reaches 0.5% for $Z/n = 14$ and 5% for $Z/n = 43$, where Z is the atomic number and n, the principal quantum number of the orbital. The 1*s* binding energy is affected by 0.5% for $Z = 19$ and by 5% for $Z = 61$.

The increased electronic charge density near the nucleus produced by the relativistic contraction of *s* and *p* orbitals causes increased screening of the nuclear charge, whence outer electrons move further away from the origin. Thus even the wave functions of *per se* nonrelativistic outer electrons, e.g. in the *d* and *f* orbitals, can be noticeably affected by relativity (Fig. 1).

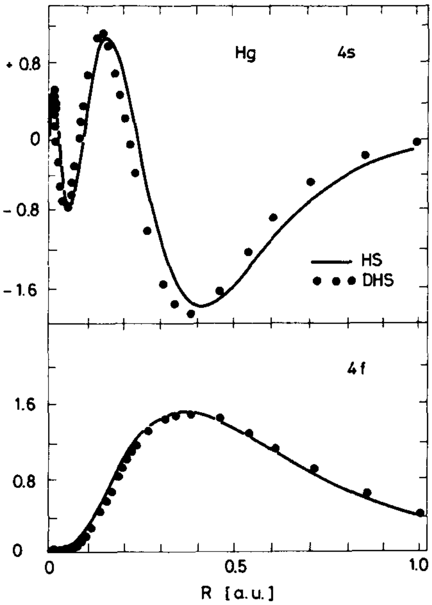

Fig. 1. Nonrelativistic Hartree–Slater and relativistic Dirac–Hartree–Slater 4*s* and 4*f* wave functions in mercury. From Ref. [28]

In addition to relativistic contraction of inner and expansion of outer orbitals, spin–orbit splitting is the second major relativistic effect in atomic structure. Neither electron orbital nor spin angular momentum alone are good relativistic quantum numbers, but the vector sum $\mathbf{j} = \mathbf{l} + \mathbf{s}$ is; the energy splitting between the two j values $l \pm s$ is a relativistic effect that can amount to several electronvolts for the valence electrons and two or three kiloelectronvolts for the 2*p* electrons of heavy atoms.

The third major relativistic factor in atomic structure is the Breit interaction, composed of current–current and retardation contributions [28]. This first dynamic correction to the electrostatic Coulomb interaction in the relativistic Hamiltonian takes account of the exchange of a single transverse photon. While it affects binding energies relatively little (even 1*s* in heavy atoms only by a fraction of one percent), it has a major impact on the separation of levels of different total angular momentum J, such as spin–orbit splittings: here the Coulomb energy cancels out, being insensitive to angular momentum, and leaves a major role to be played by the Breit interaction.

The radiative corrections of quantum electrodynamics can be of comparable magnitude as the Breit energy and must also be taken into consideration if one wishes to determine level energies to high precision. The radiative corrections comprise the self energy and vacuum polarization (of opposite signs), which together cause the Lamb shift [30]. In Fig. 2 we plot the relative contributions of Breit energy and radiative corrections to the atomic 1*s* level energy, as a function of atomic number.

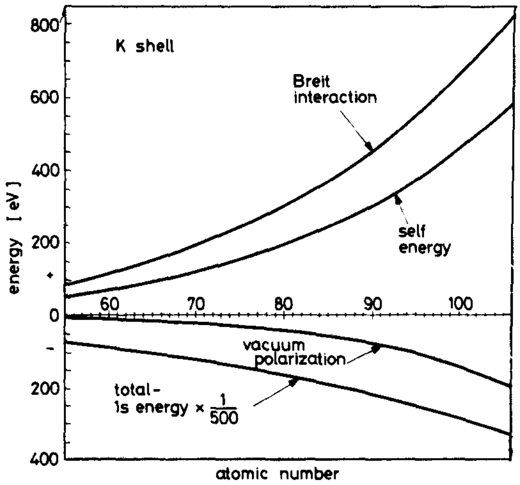

Fig. 2. Shifts produced in the K binding energies of heavy atoms by the Breit interaction, self energy, and vacuum polarization. From Ref. [30]

Transition rates are influenced by relativity due to several factors [30]. These include (i) changes in transition energies, (ii) differences between relativistic and nonrelativistic wave functions: orbital effects caused by the inclusion of the mass-velocity correction, the Darwin term, and the spin–orbit interaction in the Dirac equations, (iii) contributions from the current–current (magnetic) interaction, and (iv) retardation of the Coulomb and magnetic interactions. By artificially including these factors one at a time in numerical calculations, each effect can be studied separately [31–33]. The total effect on, for example, radiationless transitions seems at first sight to be perplexingly uneven; it can be understood, however, by considering how the orbital, current–current interaction, and retardation effects add up in magnitude and phase for both direct and exchange transitions [28].

From an extensive and systematic study of relativistic radiationless transitions, we can deduce some general trends [34]: (i) The orbital (wave function) effect tends to predominate when outer shells are involved; (ii) retardation and magnetic interaction are important for inner shells; (iii) cancellations can greatly reduce the effects of relativity, and (iv) weak transitions can be much more strongly affected by relativity than intense transitions.

2.2. Level energies

Atomic and molecular level energies (hole-state energies or electron binding energies) can in general be significantly affected by relativity, relaxation, finite nuclear size, the quantum electrodynamic corrections discussed above, coupling, correlations, and interaction with radiationless continua [36–38]. Considerable information on these complex factors can be derived from measurements with synchrotron radiation ranging from straightforward photoelectron spectrometry to some of the more sophisticated approaches mentioned in Section 1.

The relativistic independent-particle model can be used to compute the zeroth-order wave functions and energies [39, 40]. Relaxation is accounted for, in the absence of shake processes, by taking the electron binding energy as the difference between the total energies of the excited ionic state and of the ground state, calculated by separate self-consistent-field procedures [38].

Magnetic and retardation contributions can be calculated by means of the Mann—Johnson transverse operator, which includes the effect of the frequency of the exchanged virtual photon [41, 28]. The limits of this approach have not yet been established experimentally.

The nucleus can be treated as a point charge, but this leads to an error of tens of electronvolts in the K-shell binding energy of the heaviest elements. While it is thus necessary to take the finite size of the nucleus into account, it is only the root-mean-square charge radius that affects the result of energy-level calculations, irrespective of the details of the assumed nuclear charge distribution [42].

The importance of the coupling scheme is worth noting. While $j-j$ coupling is natural in relativistic calculations, this is ill-suited for most open outer shells, in which the electrostatic interaction between electrons dominates over the spin–orbit interaction. The suitble scheme for coupling electrons in these open shells thus is LS, which can be implemented by means of the relativistic LS-average scheme [39].

The effects of electron–electron Coulomb correlation on energy levels can be crudely divided into those of ground-state correlation and of dynamic relaxation. The former is essentially the result of broken pairs: there are more pairs in the ground state than in the excited state, whence the binding energy is increased. This effect can be evaluated as a sum of pair energies that survive after cancellation between ground and hole states [43].

A leading type of dynamic relaxation is the interaction with the Auger continuum that affects hole-state levels subject to Coster–Kronig decay. For these levels, fluctuations to virtual Coster–Kronig states will reduce the binding energies. This type of interaction is the radiationless many-body analog of the electron self energy. It can be treated on the basis of an approach devised by Fano already in 1961 [44] and more recently applied to the problem of Coster–Kronig fluctuations [45].

The theory of correlations is difficult and as yet in a somewhat primitive state. There is no suitable unified relativistic theory of correlations; one is forced to rely on an additive approach in which each effect is calculated separately; moreover, the prevalent nonrelativistic treatment is primarily suited for light atoms only.

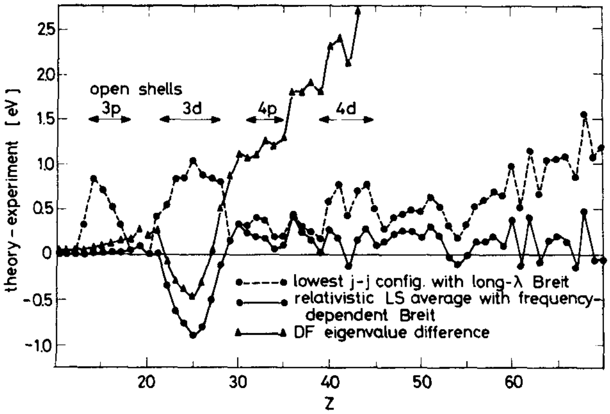

Fig. 3. Differences between calculated and measured spin-orbit splittings between $2p_{1/2}$ and $2p_{3/2}$ hole-state energies, in eV, as functions of atomic number Z. Theoretical energies were calculated in terms of the lowest $j-j$ configuration with the long-wavelength approximation for the Breit interaction (solid circles linked by dashed curve) and from the relativistic LS average with the frequency-dependent form of the Breit interaction (Mann–Johnson operator) (solid circles linked by solid curve). For comparison, the splittings from Dirac–Fock eigenvalues are also shown (triangles linked by solid curve). From Ref. [37]

The magnitude of some of the effects discussed here can be appreciated by comparing calculations with selected results from electron spectrometry [37]. In Fig. 3, we plot the differences between calculated and measured $2p$ spin–orbit splittings as a function of atomic number. The Dirac–Fock eigenvalue differences quickly go off scale, primarily because the Breit energy is not included which plays a major role in the splittings, in which the static Coulomb interaction cancels out. When the frequency-dependent Breit interaction is included and coupling is expressed in terms of the relativistic LS average, calculated splittings agree to within 0.5 eV with measurements up to $Z = 70$. (The discrepancy in the $3d$ open-shell region is well-understood as due to the exchange splitting [46], which is not included in these calculations).

A further comparison between present measurements and state-of-the-art calculations is shown in Fig. 4 for $1s$ and $2s$ binding energies [37]. For the $2s$ level,

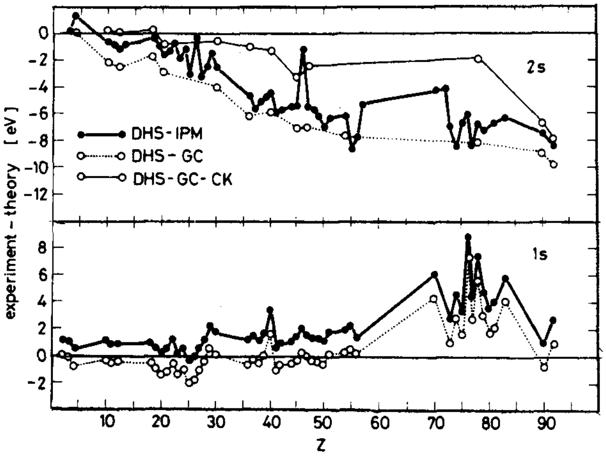

Fig. 4. Differences between measured and calculated K (1*s*) and L_I (2*s*) electron binding energies (in eV), as functions of atomic number *Z*. Theoretical energies were calculated from the relativistic independent-particle model alone (DHS–IPM), with inclusion of ground-state correlation (DHS–GC), and with inclusion of ground-state correlation as well as (super-) Coster–Kronig fluctuations (DHS–GC–CK). Energies are plotted as functions of atomic number *Z*. Curves are drawn as guides for the eye only. From Ref. [37]

inclusion of ground-state correlation and Coster–Kronig fluctuations is seen to reduce the difference between experiment and theory to approximately 2 eV up to $Z = 78$ (where the 2*s* energy is 13.9 keV); above this atomic number, uncertainties in the screening of the self energy becomes the dominant cause of the discrepancy. Valuable insights can be expected from future work on these high-*Z* level energies, with measurements primarily based on electron spectrometry with synchrotron radiation.

3. Relativistic chemistry

Relativity makes gold yellow and noble, and different from silver; it makes mercury liquid at room temperature and the mercurous ion extra-stable [47, 48]; yet, Pyykkö and Desclaux in a well-known paper noting these facts [47] comment: "most of the existing theoretical chemistry refers to an imaginary world where *c* would be infinite." Although this statement was made some eight years ago and considerable progress has been made since then [49], it probably still is true to a considerable extent. The main reason is the difficulty inherent in fully relativistic calculations of atoms and, even more so, of molecules.

In fact, no completely correct Hamiltonian exists to describe the interaction between two relativistic electrons [50]. Often it is therefore preferable to use the nonrelativistic Schrödinger equation and add on relativistic correction terms, using perturbation theory to use the "Pauli limit" operators for the mass correction, the Darwin term, and the spin–orbit and spin–other–orbit interactions. For heavy elements, however, or when highly precise results are needed, there is little choice but to turn to fully relativistic theory based on the Dirac equation.

Fundamental unresolved problems remain in the relativistic theory of many-electron systems [51, 52]. Nevertheless, from a practical point of view for atomic structure calculations, the multiconfiguration Dirac–Fock (MCDF) method offers an effective way of including relativistic effects [38]; quantitative predictions based on this method have become enormously much easier to make in recent years, owing to the ready availability of codes like those of Desclaux [53] and Grant et al [54, 55] and of suitable large-scale computing facilities.

Relativistic effects on atomic orbitals clearly can play an important role in determining molecular and chemical properties by affecting such quantities as bond length, molecular binding energies, bonding characteristics and ionization potentials. Among the best known examples are the chemical properties of gold and mercury. The chemical difference between gold and silver is now understood to be largely a relativistic effects [56–59]. The Hg_2^{2+} ion, isoelectronic with Au_2, would not exist as a stable aqueous ion in nature without the relativistic stabilization by about 1.0 eV of the bond [49]. The contraction of the filled $6s$ orbital makes Hg a more noble element than the preceding group $2B$ elements Zn and Cd [59], and relativistic effects decrease the van der Waals interatomic potential between two mercury atoms by an estimated 45% [48]. An interesting item related to the putatively stable superheavy elements is the prediction by Pitzer [60] on grounds of relativistic arguments that element 112 is likely to be extremely volatile and chemically inert, and that elements 114 and 118 may also be relatively inert gases.

In summary it appears that the importance of relativistic effects, long appreciated in atomic physics, is increasingly being realized in molecular and chemical physics. Despite the difficulties in treating much more complex systems relativistically, obstacles are being overcome with the aid of advanced theoretical approaches and greatly enhanced computing facilities. Synchrotron radiation povides unprecedented opportunities to perform the highly sophisticated measurements that are required to test theoretical advances in this fertile area of investigations.

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