Theoretical Model of Inner-Shell Excitation by Outer-Shell Electrons

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An analysis shows that atomic inner-shell states can be strongly excited by coherently driven outer-shell electrons. A time-dependent Hartree-Fock treatment illustrates the nature of this nonlinear intershell coupling. A substantial fraction of the absorbed energy can be channeled into inner-shell excitation.

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Experimental studies[1,2] of the coupling of intense radiation to atoms have indicated that it may be possible to excite atomic inner-shell levels through ordered[3] radiatively driven motions in outer shells.

An analysis of inner-shell excitation,[3] based on an analogy with atomic interactions in energetic ($v/c \sim \frac{1}{10}$) atom-atom collisions,[4,5] has been presented. Related phenomena involving multiphoton excitation and the ionization of many-electron atoms in strong electromagnetic fields have been formally treated by a time-dependent Hartree-Fock (TDHF) theory.[6] This Letter extends that theory to describe inner-shell excitation. We show that, if we assume a coherent (collective) nonlinear motion of an electronic (outer) shell produced by interaction with an external driving field, both the probability for excitation of inner-shell electrons and the quantum-state specificity can be estimated.

A simplified derivation of the theory which uses neutral xenon as an example is given. The $n=5$ shell ($5s^2 5p^6$) is designated as the outer shell, and the $4d^{10}$ shell, to which the former is closely coupled,[7] is denoted as the inner shell. The remaining strongly bound electrons that form the [Kr]-like core are treated as an equivalent potential. In the TDHF formalism, the many-body wave function describing the outer and the inner shells is given as a single Slater determinant,

$$\Psi_{\mathrm{TDHF}} = \sum_p (-1)^p \prod_{i=1}^{K} \Psi_i(\mathbf{r}_{p(i)},t), \tag{1}$$

in which p is a permutation of the indices i of the K ($=18$) electrons. The single-particle wave functions satisfy equations which are, in the dipole approximation with the neglect of spin-orbit and other relativistic effects, written as

$$i\hbar \frac{\partial \Psi_i(\mathbf{r},t)}{\partial t} = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(r) + V_{\mathrm{C}}(\mathbf{r},t) + V_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r},t) - e\mathbf{r}\cdot\mathbf{E}(t) \right] \Psi_i(\mathbf{r},t). \tag{2}$$

The laser field is a classical wave given by

$$\mathbf{E}(t) = \mathbf{E}_0(t)\cos\omega t, \tag{3}$$

and the self-consistent Coulomb V_{C} and exchange $V_{\mathrm{xc}}^{\mathrm{LDA}}$ potentials are defined, in the local-density approximation,[8] by

$$V_{\mathrm{C}}(\mathbf{r},t) = \int d^3r' (e^2/|\mathbf{r}-\mathbf{r}'|) n(\mathbf{r}',t), \tag{4}$$

$$n(\mathbf{r},t) = \sum_{i=1}^{K} |\Psi_i(\mathbf{r},t)|^2,$$

$$V_{\mathrm{xc}}^{\mathrm{LDA}}(\mathbf{r},t) = \partial[n(\mathbf{r})E_{\mathrm{xc}}(n(\mathbf{r}))]/\partial n(\mathbf{r}), \tag{5}$$

in which $E_{\mathrm{xc}}(n(r))$ is the exchange energy of a uniform electron gas with the same density. $V(r)$ is the potential produced by the ionic [Kr]-like core. These equations are manifestly nonlinear in the applied electromagnetic field.

Since the incident electromagnetic field has a slowly varying envelope, both its amplitude $\mathbf{E}_0(t)$ and frequency ω remain approximately constant over many light periods. Therefore, the Hamiltonian, Eq. (2), is almost periodic with period $T = 2\pi/\omega$ and its corresponding stationary states satisfy the quantum-mechanical Floquet theorem,[9,10] as do also the individual single-electron wave functions. Thus,

$$\Psi_i(\mathbf{r},t) = \exp(-i\Omega_i t)\phi_i(\mathbf{r},t),$$
$$\phi_i(\mathbf{r},t+T) = \phi_i(\mathbf{r},t), \tag{6}$$

in which the Ω_i are Floquet exponents with corresponding quasienergies $\hbar\Omega_i$. The functions ϕ_i can be

expanded in a Fourier series as

$$\phi_i(\mathbf{r},t)=\sum_n \phi_i^n(\mathbf{r})\exp(-in\omega t), \tag{7}$$

a form which shows that Ψ_{TDHF} is comprised of exponential terms $\exp[-i(\sum_{i=1}^{K}\Omega_i+n\omega)t]$ with n an integer.

We now introduce an important approximation and adopt a "shell model" which *separates* the treatment of the outer-shell electrons from those of the inner shell and assume that the $4d^{10}$ inner-shell electrons remain frozen in their ground state. The TDHF equations (1)–(5) then are written for $K=8$ with the inner-shell electrons counted in the core. For a weak incident field this is a good approximation in xenon from detailed calculations involving linear-response theory.[11,12] The potentials V_C and V_{xc}^{LDA} are calculated with use of only the outer-shell wave functions and are represented as an external potential U given by

$$U(\mathbf{r},t)=V(r)-e\mathbf{r}\cdot\mathbf{E}(t)+V_C(\mathbf{r},t)+V_{xc}^{LDA}(\mathbf{r},t), \tag{8}$$

with the corresponding Fourier analysis

$$U(\mathbf{r},t)=\sum_{k=1}^{\infty} U^k(\mathbf{r})\cos(k\omega t+\theta_k). \tag{9}$$

Importantly, the Floquet exponent disappears and the time dependence comes directly from the various components of Eq. (7). In particular, if Ψ_i^n has large Fourier components for indices $n=0$ and M, V_C and V_{xc}^{LDA} have correspondingly large Fourier components for integral indices occurring between $-M$ and $+M$. Therefore, this potential will cause transitions in the inner shell when the excitation energy E satisfies the condition $E=n\hbar\omega$ for $n\leq M$. The resulting transition rate, from perturbation theory, is

$$w(E)=(2\pi/\hbar)|S_n(E)|^2\delta(E-n\hbar\omega), \tag{10}$$

in which the transition amplitude $S_n(E)$ is calculated below.

We denote the inner-shell matrix elements of U^k by

$$U_{ij}^k=\int d^3r\,\langle\Psi_j(\mathbf{r})|U^k(\mathbf{r})|\Psi_i(\mathbf{r})\rangle, \tag{11}$$

in which Ψ_i are a complete set of Hartree-Fock wave functions for the inner shell, including levels in the continuum, with r symbolizing all inner-shell coordinates. In nth order, we obtain

$$S_n(E)=U_{0E}^n+\sum_{k_1+k_2=n}\sum_i\frac{U_{0i}^{k_1}U_{iE}^{k_2}}{E_0-E_i-k_1\hbar\omega}+\ldots+\sum_{\substack{i,j,\ldots,s\\ [n-1\text{ indices}]}}\frac{U_{0i}^1U_{ij}^1\cdots U_{sE}^1}{(E_i-E_0-\hbar\omega)(E_j-E_i-\hbar\omega)\cdots(E_s-E_r-\hbar\omega)}, \tag{12}$$

with the summations denoting the sum over bound levels and integral over continuum states. In general, all orders in this expression must be retained, since the U^k are of kth order in the field so that all terms are nth order. It is clear by inspection that the first term corresponds to "internal nth-order harmonic generation" while the last one corresponds to "lowest-order perturbation theory" with the external field screened by the outer electrons. Perturbatively, consecutive orders of U^k are related by

$$U^k/U^{k-1}\simeq\mu_{os}E/\Delta E_{os}, \tag{13}$$

in which μ_{os} is a typical outer-shell dipole matrix element and ΔE_{os} is an energy scale characterizing outer-shell excitations. Therefore, amplitudes in successive orders are related approximately by $\Delta E_{os}/(E_i-E_j-k\hbar\omega)$. Since inner-shell energy spacings are typically larger than those of an outer shell, higher orders in the perturbation are generally diminishing except in cases possibly involving intermediate resonances. Therefore, if there is a resonance at $k\hbar\omega$, a large dipole moment can appear at that harmonic frequency.

The behavior of the single-electron wave functions of the outer shell, $\Psi_i(r,t)$, is now investigated. Since the atomic response in an adiabatically applied monochromatic field is sought, we seek the solution of the TDHF equations [Eqs. (1)–(7), $K=8$] that correlates adiabatically to the $5s^25p^6\,{}^1S_0$ ground state. For weak fields and sufficiently low frequencies, the response of each electron is similar to that of a harmonic oscillator with a resonance energy equal to that of the first excited state $\hbar\omega_0$ (8–9 eV in xenon). Therefore, the perturbation parameter from Eq. (13) is

$$B=\frac{1}{4}\frac{\mu_{os}E_0}{\Delta E}=\frac{1}{4}\frac{\alpha(\omega)E_0^2}{\hbar\omega_0}\left(\frac{\omega_0^2}{\omega_0^2-\omega^2}\right), \tag{14}$$

in which $\alpha(\omega)$ is the atomic polarizability (per electron), a quantity which can be calculated by linear-response theory.[11,12] However, the harmonic-oscillator model must be used cautiously, since the potential is actually anharmonic. A single excited electron escapes if it is excited above the ionization potential V_0. For simplicity in the following, we ignore possible complications arising from autoionizing resonances. In consideration of the results given by Eqs. (6) and (7), if $\hbar(\Omega_i+n\omega)\geq V_0$, $\phi_i^n(r)$ is a continuum wave function, but note that this relation has to be modified in strong fields, as discussed below.[13]

In the harmonic-oscillator model, the amplitudes $|\phi_i^n|^2$ are proportional to B^n for $B \ll 1$, so that the probability of ionization is in accordance with lowest-order perturbation theory. For a sufficiently strong field, $B > 1$, the higher-harmonic components acquire large magnitudes, the self-consistent potential becomes appreciably modified, and the ionization of the lowest ϕ_i^n levels can be suppressed.[2,6,13,14] The criterion[13] for the disappearance of the nth channel for ionization, due to electron trapping by the ponderomotive potential, is

$$n\hbar\omega - V_0(E_0) < \frac{1}{4}\frac{E_0^2 e^2}{m\omega^2}, \tag{15}$$

in which $V_0(E_0)$ is the ionization energy of the atom modified by the ac Stark effect. Significantly, both the disappearance of the lowest-energy electrons and the persistance of the higher-energy peaks have been observed[2,15] in agreement with Eq. (15). In xenon[2] at 193 nm, electron trapping of the two-photon ($n=2$) peak occurs at an intensity of 2×10^{14} W/cm^2 according to Eq. (15). However, the onset of strong nonlinearity arises at an intensity of 1.2×10^{15} W/cm^2, the value for which $B=1$ in Eq. (14). The combined effect causes the single-electron wave function to have a sizable $n=2$ component that does *not* ionize. The $n>2$ components, of course, will still consist partly of outgoing waves. If we *assume* a coherent outer-shell motion, a reasonable approximation for the bound part of the TDHF wave function that correlates to the ground state is a symmetric product of wave functions for the six $5p$ electrons of the form[6]

$$\Psi_i(\mathbf{r},t) = \exp(-i\Omega_i t)[\phi_i^0(\mathbf{r}) + \phi_i^1(\mathbf{r})e^{-i\omega t} + \phi_i^2(\mathbf{r})e^{-2i\omega t}]. \tag{16}$$

The norms of the Fourier components,

$$P_n = \int |\phi_i^n(\mathbf{r})|^2 d^3r, \tag{17}$$

were calculated for a one-dimensional harmonic oscillator with polarizability and resonance frequency corresponding to those of xenon. For an intensity of 4.5×10^{14} W/cm^2 and frequency $\omega=0.7\omega_0$, the values are $P_0=0.246$, $P_1=0.330$, $P_2=0.234$, and $P_3=0.116$, respectively.

Two important conclusions emerge. First, if we interpret P_n as the probability of an individual electron being "dressed" by n photons, the $5p^6$ shell of xenon has a sizable amplitude for virtual excitation with twelve photons,[16] an energy sufficient to eject a $4d$ electron, at an incident 193-nm laser intensity in the range of $\sim 4\times10^{14}$ W/cm^2. Significantly, this value is in reasonable agreement with that observed[2] in the electron spectrum of xenon for the onset of strong nonlinear coupling. Second, the results show that the potential U produced by these electrons contains predominantly the first and second harmonic components. This is *exactly* the expected characteristic of a coherent ordered motion of the outer-shell electrons.

An estimate can be made of the inner-shell excitation due to the potential U. The xenon $4d^{10}$-ionization thresholds are 67.55 eV ($4d_{5/2}$) and 69.52 eV ($4d_{3/2}$). When the $n=2$ terms get large, the dominant lowest-order terms in the perturbation analysis [Eq. (12)] can be cast in a form in which the individual terms are written as $(\mu E_2/\hbar\Delta\omega)^2$, for which μ is an inner-shell dipole matrix element, E_2 is the field at 2ω induced by the outer shell, and $\hbar\Delta\omega$ is an appropriate energy denominator. With use of $\mu^2 = f(ea_0)^2(\mathcal{R}/\hbar\omega_1)$, with $\mathcal{R}=13.6$ eV, $\hbar\omega_1$ an inner-shell excitation energy, and f the oscillator strength of the transition, the square of the matrix elements of Eq. (11) becomes

$$|\langle|U|\rangle|^2 \simeq \left(\frac{E_2}{E_a}\right)^2 \frac{4f\mathcal{R}^3}{(\hbar\Delta\omega)^2(\hbar\omega_1)}, \tag{18}$$

with $E_a = e/a_0^2$.

Bounds for E_2/E_a follow. A high estimate, $E_2/E_a=1.4$, is derived on the assumption of an oscillating charge of $2e$ at $2\omega_1$ corresponding to the parameters $P_0=P_1=P_2=\frac{1}{3}$ for the six $5p$ electrons and a mean distance of $1.2a_0$ between the outer and inner shells. The latter is derived from a density-functional calculation of xenon.[12] A low estimate of $E_2/E_a=0.17$ is obtained by scaling of the static shielding field calculated in Ref. 12 around the position of the peak density of the $4d$ shell ($0.8a_0$). Obviously, better theoretical knowledge of this number is crucial. Fortunately, the structure of the excited levels of the $4d^{10}$ shell of xenon is well known.[17] Two different classes of terms are considered, namely (a) those in the continuum with $f=11$ and $\hbar\omega_1 \sim 100$ eV and (b) one resonant level at 65.1 eV corresponding to the $4d^{10}5s^25p^6 \rightarrow 4d^95s^25p^2(^2D_{5/2})6p$ transition with $f=0.02$. The latter transition can experience shifts due to outer-shell "vacancies" and the (shielded) external field. Taking the higher estimate for E_2, we get $|\langle|U|\rangle|^2=0.29$ with the continuum as the intermediate state and $|\langle U|\rangle^2=7.6$ for the resonant level which corresponds to ten photons absorbed. The latter value simply signifies saturation and that the appropriate magnitude to use is unity.

The simplest perturbation calculation relates the probability of inner-shell ionization P(Auger) to that of the absorption $P(4\omega)$ which corresponds to the absorption of four photons by a single electron.[15] We assume that both these processes have the same density of final states and the same bound-continuum matrix elements. This ratio then reduces to a product of four expressions of the type $|\langle|U|\rangle|^2$. With the use of the estimates given above, the ratio of probabilities P(Auger)$/P(4\omega)=0.15$ is obtained. This magnitude indicates than an appreciable fraction of the absorbed

energy can be channeled into the excitation of inner-shell states.[1-3]

A treatment has been presented that calculates the probability of inner-shell excitation arising from coherently driven ordered motions of an outer shell. Consequently, it is important to understand the physical conditions[2] governing the existence of a coherent multielectron excitation of an atomic outer shell. For this question, TDHF calculations can set a limit. In the regime for which those calculations predict single-electron excitations, in particular, close to a resonance, no coherent excitation will occur. Of course, the residual interaction among the outer-shell electrons represents a mechanism for damping of the coherent motion that requires further investigation. Although a theoretical framework is known[18] which can be used to appraise these effects, that calculation falls outside the domain of the TDHF theory.

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[1]T. S. Luk, U. Johann, H. Egger, H. Pummer, and C. K. Rhodes, Phys. Rev. A **32**, 214 (1985).

[2]U. Johann, T. S. Luk, H. Egger, and C. K. Rhodes, Phys. Rev. A (to be published).

[3]K. Boyer and C. K. Rhodes, Phys. Rev. Lett. **54**, 1490 (1985).

[4]J. S. Briggs and K. Taulbjerg, in *Structure and Collisions of Ions and Atoms,* edited by I. A. Sellin (Springer-Verlag, Berlin, 1978), p. 105.

[5]C. Bottcher, J. Phys. B **10**, L445 (1977).

[6]A. Szöke, Phys. Rev. A (to be published).

[7]G. Wendin, Struct. Bonding (Berlin) **45**, 322 (1981).

[8]W. Kohn and P. Vashishta, in *Theory of the Inhomogeneous Electron Gas,* edited by S. Lundqvist and N. H. March (Plenum, New York, 1983), p. 79.

[9]Ya. B. Zel'dovich, Usp. Fiz. Nauk **110**, 139 (1973) [Sov. Phys. Usp. **16**, 427 (1973)].

[10]S.-I. Chu, Adv. At. Mol. Phys. **21**, 240 (1984).

[11]M. J. Stott and E. Zaremba, Phys. Rev. A **21**, 12 (1980).

[12]A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).

[13]A. Szöke, J. Phys. B **18**, L427 (1985).

[14]H. G. Muller, A. Tip, and M. J. van der Wiel, J. Phys. B **16**, L679 (1983); H. G. Muller and A. Tip, Phys. Rev. A **30**, 3039 (1984).

[15]P. Kruit, J. Kimman, H. G. Muller, and M. J. van der Wiel, Phys. Rev. A **28**, 248 (1983).

[16]The equivalence of P_n with the probability of "dressing" or "virtual absorption" of n photons is discussed, e.g., by L. Rosenberg, in *Advances in Atomic and Molecular Physics,* edited by D. Bates and B. Bederson (Academic, New York, 1982), Vol. 18, p. 1.

[17]S. Southworth *et al.,* Phys. Rev. A **28**, 261 (1983); D. L. Ederer and M. Manalis, J. Opt. Soc. Am. **65**, 634 (1975).

[18]T. N. Chang and U. Fano, Phys. Rev. A **13**, 263, 282 (1970); M. Baranger and I. Zahed, Phys. Rev. C **29**, 1005, 1010 (1984).