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Dispersion of an atomic, giant-dipole resonance

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The dispersion of the collective excitation in the $n=4$ shells of xenon has been calculated, including all significant partial-wave contributions, by a time-dependent, self-consistent-field method. The calculation reveals details of the physical mechanism that produces the dispersion. The calculated dispersion coefficient is compared with experimental results.

I. INTRODUCTION

This paper reports the first time-dependent, self-consistent-field[1] calculation of finite-wavelength spectra for xenon. It adds substantially to the understanding of the dispersion of the strong collective mode that dominates the spectra in the regions of $4d$-shell excitations. That mode is a dipole oscillation of the charge in the $n=4$ shells. The collective peak disperses to higher energy as the wavelength of the applied field decreases. The calculated dispersion coefficient is compared with existing data. The calculation challenges experimenters to generate more and better data. It also identifies precisely what it is, in the interaction between the $n=4$ shells of the atom and the applied fields, that produces the dispersion.

The observed spectrum[2] of photoabsorption by the $4d$ shell of xenon to the continuum differs from the predictions of simple calculations of atomic structure. The calculations give a monotonically decreasing function of energy from 1 Ry above threshold. In the data there is a peak about 2 Ry wide centered at 7.5 Ry excitation energy, or about 3 Ry above the $4d$ threshold. Most of the oscillator strength of the $4d$ shell is in this peak. Zangwill and Soven (ZS) showed that a time-dependent, self-consistent-field calculation of the spectrum gives good agreement with the observed photoabsorption.[1] They showed evidence that the peak is an atomic, giant-dipole resonance, that is, a collective oscillation of the charge in the $n=4$ shells of the atom. It is strongly damped, as the width of the peak proves. This is reasonable, since its energy is degenerate with a continuum of one-electron excitations. The charge fluctuations and the induced fields they produce are dominated, at energies near the peak, by the contributions from the $n=4$ shells. The spatial distribution of the induced charge is consistent with a simple picture of charge sloshing back and forth across the atom.[3]

The excitations of $n=4$ electrons in xenon and in similar atoms can be measured by electron-energy-loss spectroscopy. At small momentum transfer q, that is, when the applied fields have long wavelength and $l=1$ angular dependence, energy-loss and photoabsorption spectra differ only by a slowly varying function of the excitation energy. As the momentum transfer increases, the wavelength of the applied fields becomes shorter and there are angular dependences other than $l=1$ present. There exist preliminary measurements of the dispersion of the collective peak for atoms near xenon in the Periodic Table.[4,5]

II. THE CALCULATION

The time-dependent, self-consistent-field calculation, extended to describe electron-impact excitations, can be tested by comparison with the data. The method of the calculation is close to that given by ZS. Consider a high-energy electron ($\approx 10^5$ eV) scattering from an atom. It is fully adequate to consider an incident plane wave and transitions to final states that are also plane waves. The atom may be excited during the transition. The Coulomb potential of the passing electron, acting on electrons bound in the atom, drives their transitions. For scattering with a particular momentum transfer $\mathbf{q}$, the Fourier transform of the Coulomb potential at wave vector $\mathbf{q}$ is the effective part of the field applied to the atom. Thus:

$$V_{\mathbf{q}}=(-4\pi e/q^2)\exp(i\mathbf{q}\cdot\mathbf{r}) \tag{1}$$

is the applied field to use in the calculation. This potential cannot exist in a vacuum; rather it implies an applied charge density $-e\exp(i\mathbf{q}\cdot\mathbf{r})$. Even those transitions that can be driven only by placing applied charge within the atom, such as monopole (breathing-mode) transitions, are observable in energy-loss spectra. It is convenient to expand the potential in spherical waves:

$$V_{\mathbf{q}}=(-4\pi e/q^2)\sum_{l=0}^{\infty}(2l+1)i^l j_l(qr)P_l(\cos\theta) \tag{2}$$

because, as ZS point out for the $l=1$ wave, the spherical symmetry of the unperturbed atom means that its response to each term in Eq. (2) may be calculated independently. For each l, an integral equation for the induced charge density with that angular dependence was solved using the method given in ZS. For each q, all important l's were included in a calculation of the spectrum. Then the dispersion of the centroid of the collective peak in the spectra was calculated.

Note that there are two ways in which dispersion may arise. Let d be a typical radius for an electron in the atomic shell being excited. First, as qd becomes comparable to 1, monopole ($l=0$), quadrupole ($l=2$), and other nondipole transitions can occur. They go to a set of final states different from those reached by dipole ($l=1$) transitions. Second, again as qd becomes comparable to 1, the wavelength of the applied field becomes comparable to the size of the atomic shell being excited. If it were not for this second effect, the response at any q could be obtained by taking an appropriate linear combination of responses to long-wavelength fields with different values of l. As it is, wavelength variations are important. At each q, the responses to the l fields must be calculated using the spherical Bessel functions that appear in Eq. (2).

This calculation, like ZS, uses local-density-approximation (LDA) wave functions for the ground-state orbitals. The results of both calculations for the $4d$ photoabsorption of xenon are in excellent agreement with data,[2] and with each other. It is possible to study the dispersion of the peak and the nature of the collective mode with the present calculation.

III. THE COLLECTIVE EXCITATION

This section describes the shape of the charge oscillations that produce the collective peak, gives the value of its dispersion coefficient, and identifies the cause of the dispersion. In the course of the calculation, one has available the contributions to each l component of the induced field from each occupied shell in the atom. At the energy of the collective peak, the $l=1$ parts of the polarizations of the ten $4d$ electrons and of the six $4p$ electrons are the source of most of the induced field, which has, therefore, an $l=1$ shape. It is as strong as the applied field. Thus the internal, restoring force on those electrons is large, produced mainly by their motion, and nearly independent of the rest of the atom. Both ZS and the present calculation show that the induced exchange and correlation forces are much smaller than the Coulomb forces that act to restore the oscillating charge. The collective excitation is an atomic, giant-dipole resonance in which the $n=4$ shell moves with respect to the nucleus and the more-tightly bound shells.

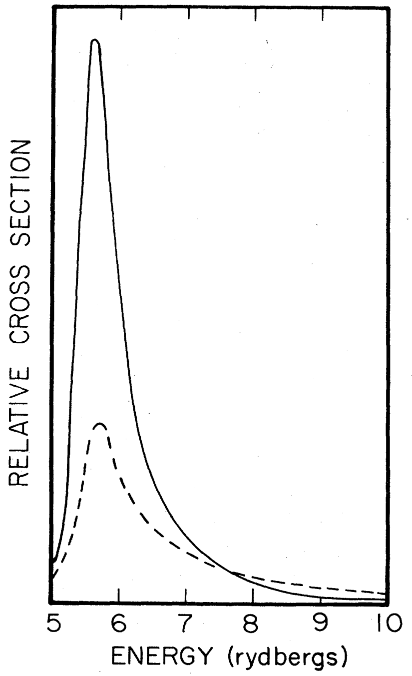

FIG. 1. One-electron calculations of electron-energy-loss spectra of xenon, for different momentum transfers q. The solid line is for $0.3\,\text{Å}^{-1}$ and the dashed for $3.4\,\text{Å}^{-1}$.

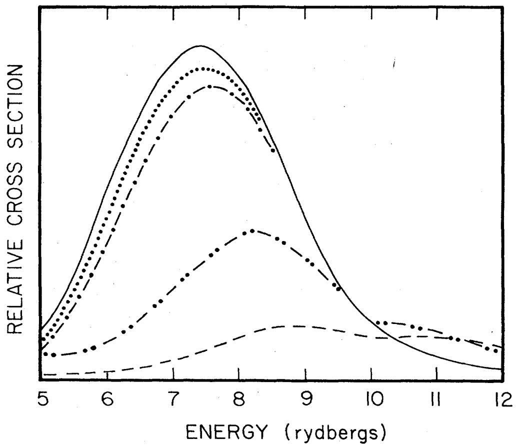

FIG. 2. Local-field calculations of electron-energy-loss spectra of xenon, for $0.3\,\text{Å}^{-1}$ (solid), $1.0\,\text{Å}^{-1}$ (dotted), $1.4\,\text{Å}^{-1}$ (dot-dashed), $3.4\,\text{Å}^{-1}$ (dot-dot-dashed), and $5.0\,\text{Å}^{-1}$ (dashed).

Figure 1 shows the one-electron result for two values of q. No induced fields were used. There is no collective peak in the curves. There is a small shift of oscillator strength to higher energies as q increases. Figure 2 shows the time-dependent, self-consistent-field results for five momentum transfers. There is a collective peak at each q. It is broad in every case, as is expected of a collective excitation that is degenerate with a continuum of one-electron excitations. Its centroid disperses to higher energy as q increases.

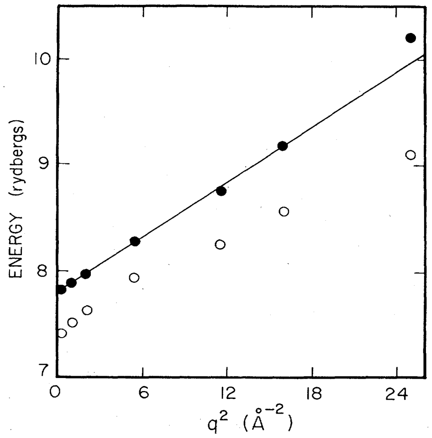

FIG. 3. The calculated dispersion of the centroid (solid circles) of the collective peak, in the electron-energy-loss spectra of the $n=4$ shells of xenon. The curves shown in Fig. 3 were used as weighting functions in calculating the average energies. The peak energies are shown by the open circles. The line has a slope of $1.2\,\text{eV}\,\text{Å}^2$, and the peak energies disperse at roughly $0.9\,\text{eV}\,\text{Å}^2$ in the range plotted.

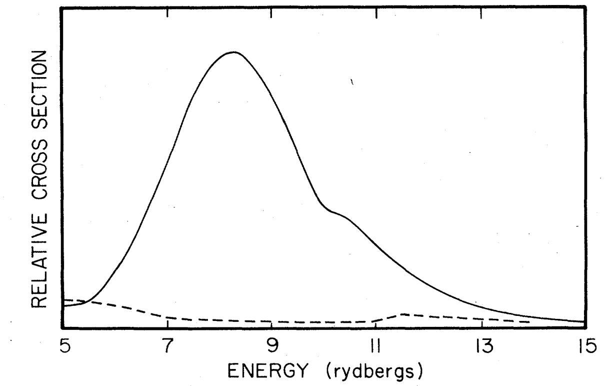

FIG. 4. Contributions to the energy-loss spectrum of xenon at 3.4 Å^{-1}. The time-dependent, self-consistent-field calculations for all the l components of the transition operator that contribute significantly are shown, as solid ($l=1$) and dashed (sum of $l=0$, 2, and 3) lines.

The energy of the centroid of the collective feature and its peak energy are linear functions of the square of the wave vector q, as Fig. 3 shows. The constant of proportionality is 0.9 eV Å^2 for the peak energy, 1.2 eV Å^2 for the centroid. This dispersion coefficient is the meeting ground between theory and experiment. To provide a scale, the ratio between the energy of a free electron and the square of its wave vector is 3.8 eV Å^2.

To learn why the centroid disperses, let us concentrate on the calculation for 3.4 Å^{-1}. Figure 4 shows all significant contributions to that spectrum, separated according to the value of l in the applied field from which they arise. Even though the product of this q with the 4d radius is about 1.7, nondipole transitions make only a small contribution to the spectrum. There is no collective peak in the $l=0$ or $l=3$ channels, and no strong one in $l=2$. The peak in the spectrum is dominated by the dipole, $l=1$ channel. The dispersion of the $l=1$ peaks is indistinguishable from that in the complete spectra of Fig. 2. The dispersion must, therefore, be a finite-wavelength effect in the $l=1$ channel, for these momentum transfers. This is partly in accord with the predictions of a simple, collective model formulated by Franck.[4,6] A sphere, containing ten electrons at the same density as is found in the 4d shell of xenon and a rigid, uniform, positive charge, has normal modes of oscillation labeled by the usual angular indices l and m.[7] Franck used the Lindhard dielectric function to describe the response of the electrons to applied fields. He found a large dispersion, 11 eV Å^2. In agreement with the present calculation, he found that finite-wavelength effects were much more important than excitations of modes with l's different from 1. The large value of his dispersion coefficient is the same as that of the bulk plasmon in an electron gas with the density of the 4d electrons in xenon. That the present calculation finds the same mechanism for dispersion, but a much smaller coefficient, suggests that the simple model may be a good one, but only if the Lindhard dielectric function be replaced by something more appropriate for describing response in a bounded system.

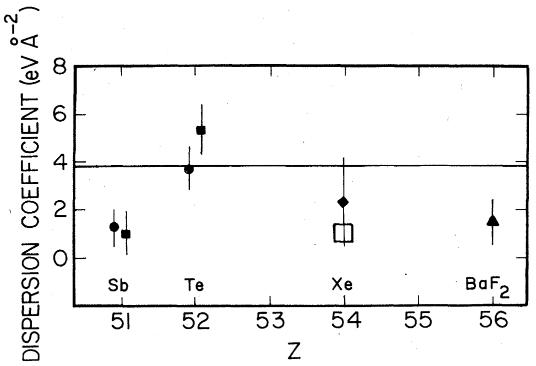

FIG. 5. Dispersion coefficients for the collective peaks associated with the filled $n=4$ shells in elements near xenon. The results of Ref. 4 are plotted vs atomic number. Their stated uncertainties are indicated. The diamond at xenon is an estimate of the dispersion in the results of Ref. 5. The horizontal line is the free-electron value and the open square at xenon is the result of the present calculation.

IV. DATA

Now let us consider the observations. Franck and Schnatterly have measured the dispersion of the collective peak associated with filled 4d shells in antimony, tellurium, and barium.[4] They used solid samples and varied the momentum transfer from small values up to 1.4 Å^{-1}. They found the dispersion of the energy centroids to be close to a quadratic function of the momentum transfer, with much scatter and large uncertainties. The dispersion coefficients they obtained are shown in Fig. 5. The tellurium samples and data were their best,[8] and fell close to the free-electron value. The coefficients for antimony and barium were smaller than the free-electron value, one-quarter to one-half of it, but with uncertainties large enough to be consistent with the value found in the present calculation, which is one-quarter of the free-electron value. Analyses in this laboratory of real and simulated data indicate that the background beneath the collective peak in energy-loss spectra also disperses, and that methods that have been used to remove that background[4] may produce some false dispersion of the peak in the data. Afrosimov, Gordeev, Lavrov, and Shchemelinin have measured energy-loss spectra of noble gases including xenon.[5] From their Fig. 2, if one ignores the problems in subtracting the background, it appears that the dispersion coefficient for the collective peak for xenon would be about 2.3 eV Å^2, near half the free-electron value. This result is included in Fig. 5.

V. CONCLUSION

This paper reports the first realistic calculation of the dispersion of a collective excitation in an atom. Over the range of wave vectors investigated, applied and induced fields with dipolar angular shape dominate the computed spectra. The dispersion of the peak is therefore a finite-wavelength effect in the $l=1$ part of the response of the atom to the applied field. The dispersion coefficient calculated is smaller than the experimental results. Better data and more painstaking analysis of it may reduce this discrepancy. They will provide a new test of time-dependent, self-consistent-field calculations of atomic spectra.

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