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Atomic clusters with nuclear methods

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I. INTRODUCTION

There are remarkable parallels between atomic clusters and atomic nuclei, and I want to explore some aspects having to do with giant resonances. For electronic properties of clusters, and particularly alkali metal clusters, the common ground is mean-field theory. In nuclei, mean-field theory gives a the shell model and the fundamental expansion to make theories of spectroscopy. But mean-field theory is also widely used in chemistry and condensed matter physics, and it provides a robust approximation in its domain of validity. Particularly successful for ground state properties is the density-functional theory [1], which treats the electron-electron interaction in a local-density approximation (LDA), i.e. by adding a density-dependent contact term to the Hartree Hamiltonian. The theory is commonly used to calculate ground state structures of molecules and condensed systems. A corresponding theory for excitations is the time-dependent local-density approximation (TDLDA), which my focus here.

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A. Why TDLDA?

Various formal justifications can be given for theory based on the TDLDA. The equation of motion is nothing more than the time-dependent Schroedinger equation in a self-consistent mean field, a time-dependent version of the Kohn-Sham equation. It can be derived from the stationary principle

$$\delta \int dt \langle \Psi | H - i\hbar \frac{\partial}{\partial t} | \Psi \rangle = 0.$$

in the same way that the static mean-field equations are derived by minimizing the energy, $\delta \langle \Psi | H | \Psi \rangle = 0$. Here $\Psi = \mathcal{A} \prod_i \phi_i$ is restricted to be a Slater determinant of single-electron wave functions ϕ_i . The formal existence proofs of Density Functional Theory can be generalized to the time-dependent problem [3].

My own optimism for the method is based on more pragmatic considerations. Provided the space of wave functions ϕ_i is not artificially truncated, the TDLDA automatically satisfies sum rules such as the TRK sum rule. Thus it will give the correct integral of a strength function. On the other hand, one can argue on grounds of adiabaticity that a theory that describes ground states should be valid also for low-frequency excitations. With these two limits respected by the theory, the theory should be a reasonable approximation to the behavior in between. This argument relies on using the same energy functional for the dynamics as was used to construct the static electronic wave function. This generalized self-consistency—using the same Hamiltonian for the dynamics as for the statics—has been a powerful principle in nuclear physics for describing the collective excitations including the giant resonances.

But one should also keep in mind that some properties are not expected to be well described in the TDLDA. And any property that depends on intrinsic two-body operators would be doubtful, because the basic approximation is a truncation to the one-particle density. We consider all properties that can be expressed with products of one-body operators to be fair game for TDLDA, including nonlinear effects of strong fields.

A number of researchers, particularly in chemistry and in condensed matter physics have taken up the TDLDA theory. The first application of TDLDA to atoms was the work of Zangwill and

Soven in 1980 [4], who calculated the photoionization cross section¹ of noble gas atoms in the energy range 15–35 eV. Since then, the nonlinear response of atoms has been examined in TDLDA [6]. Improved treatments of the Coulomb field in TDLDA for noble gas atoms were given in a phenomenological way in ref. [7] and with an extended functional in ref. [8]. It is interesting to note that Kohn and collaborators recently advocated using the real-time technique for the calculation of the van der Waals interaction between atoms [9].

The first application of TDLDA to molecules was a study of N₂ and C₂H₂ by Levine and Soven [10]. Extensive RPA calculations for larger systems have been carried out by the Scandinavian groups of H. J. A. Jensen and H. Ågren the atomic orbital representation [11,12]. The TDLDA has also been applied by two North American quantum chemistry groups to study the excitations of small molecules [14–16].

On the other extreme in size is bulk matter, and here the method has been applied to semiconductors, insulators, and simple metals. The agreement is good in diamond and Si (10%) and somewhat worse in Ge (25%), with the theory always giving too much screening [17]. The TDLDA plasmon dispersion was calculated for alkali metals in ref. [18]. The theory does well for Al and Na, but becomes increasingly poor for heavier alkalis, failing to reproduce the anomalous dispersion in Cs. The dielectric function of TDLDA has also been used in the construction of sophisticated theories of the single-electron Green's function [19].

The TDLDA applications to clusters include many publications in which schematic treatments of the atoms, such as the jellium model, were employed. Calculations with realistic atomic Hamiltonians have been started only recently. Besides our own work, described below, a Spanish group has started calculations on alkali clusters [20] using the Berkeley computer codes that were written for condensed matter. Our own method has been taken up by the European groups of Reinhard and Suraud [21], who so far have applied the method to sodium clusters. The first

¹Their numerical algorithm, using a Green's function in a radial coordinate mesh, was in fact identical to one used earlier in nuclear physics to treat RPA in the continuum [5].

calculation of the C_{60} absorption spectrum with a realistic Hamiltonian was by Broglia's group, using the matrix RPA representation [22].

There are of course much more accurate theories that have a corresponding penalty in computational effort required. In quantum chemistry, the configuration interaction (CI) approach is systematic and has reached very high accuracy for small molecules, but the scaling of computational effort with size is very poor. Other theories include the so-called GW approximation of condensed matter physics as well as the many-body perturbation formalism that is often applied in atomic physics. However, the GW approximation apparently has not led to a better theory of the dielectric response; ref. [24] states,

"The GW eigenvalues would lead to an apparent overcorrection of the dielectric function from too large (in LDA) to too small."

On the other hand, the many-body perturbation theory has been very successful in the atomic problem [25]. With an accurately calculated nonlocal Σ [43], the theory gives transition strengths in IB atoms that agree well with experiment, better than TDLDA [42].

B. Numerical method

There are many ways to implement the TDLDA equations. Our numerical calculations use the algorithm developed for nuclear theory by Flocard, et al. [2]. Rather than transforming to a frequency representation as is commonly done, one solves TDLDA equations in real time. We have found this technique to be competitive with many techniques in current use, and it gives us the tool to make systematic surveys. The algorithm uses a three-dimensional coordinate space mesh to represent the electron wave functions. This has the advantage that the Hamiltonian matrix is sparse if one uses a difference formula to represent the kinetic energy operator [26,27]. One trick to achieve good accuracy in a coarse mesh is to use a higher-order difference formula [2,26]. As a first stage in a calculation, the static mean-field equations are solved iteratively to generate a stationary wave function. Then the wave function is perturbed by an external field, $\phi' = e^{iQ(r)}\phi$, and the subsequent evolution in time is computed with the operator, $\phi(t) = exp[-i \int^t H(t)dt]\phi'$, where

$H(t)$ is the Kohn-Sham Hamiltonian evaluated with the instantaneous density. The numerical algorithm for the evolution operator same as in ref. [2]. It is very stable, provided the time step is smaller than the largest eigenvalue of the Hamiltonian. Physical quantities are extracted from expectation of observables Q' as a function of time. This can be expressed formally as the correlator, $\theta(t)\langle[Q'(t), Q(0)]\rangle/i$.

In the real-time implementation of the TDLDA, the computing effort scales with the number of particles N and the number of mesh points D as $ND \sim N^2$. Methods using either a particle-hole representation or the response formalism scale as a higher power, at least if one applies the methods naively without truncation of matrix diagonalization or inversion operations.

As mentioned above, we are not interested in exploring a large set of energy functionals, and we have settled on one that has been widely applied for structure calculations. This uses the local density exchange-correlation functional of Perdew and Zunger [28]. The ionic pseudopotentials are constructed with the prescription of [29], treating nonlocality effects with the method of Kleinman and Bylander [30]. An obvious improvement for systems with unpaired spins is the local spin-density approximation. There are promising new energy functionals, particularly the so-called Generalized Gradient Approximation (GGA) exchange-correlation energy [31,32].

C. A sampler of results

So far we have completed studies on the optical absorption spectra of alkali metal clusters and various carbon structures, including carbon clusters, C_{60} , and conjugated carbon molecules. Briefly, our main physics results are:

- 1) Extension by an order of magnitude of the masses that can be calculated with realistic Hamiltonians; we reported Na and Li up to $N = 140$ (ref. [33]).
- 2) Demonstration that the theory works well for large Li clusters. We confirmed results of less realistic models [34–36] that attributed the large red shift of the surface plasmon to the effective mass enhancement caused by the pseudopotential. The theory also reproduces the rather broad, asymmetric shape of the plasmon peak, thus showing that the width in this system is due to what is

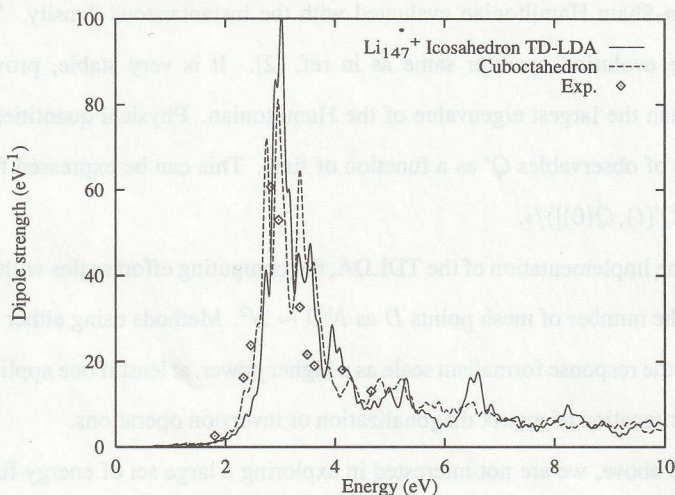


FIG. 1. Optical absorption of Li_{147}^+ clusters, from ref. [33]

called Landau damping in the many-body community and interband transitions in the condensed matter community. See Fig. 1.

3) In sodium clusters, we confirmed the early jellium studies that predicted the surface plasmon frequency that was too high by 10%. There is a recent report that the TDLDA agrees with the experiment [20], but it is now believed that the method used there, a supercell technique, was not fully converged due to dipole-dipole interactions between clusters in different cells [37].

4) First calculation of the optical spectra in carbon structures extending from the optical to the VUV region, and including the $\sigma-\sigma^*$ together with the $\pi-\pi^*$ manifolds of states [38,39].

5) Good agreement between theory and experiment for the optical absorption spectrum in benzene [39]. See Fig. 2.

6) One of very few realistic calculations of the C_{60} optical absorption [33,22,39] This is a challenge because the screening from the $\sigma-\sigma^*$ manifold must be taken into account to reproduce the observed strengths in the nominally $\pi-\pi^*$ transitions. The integrated strength is shown in Fig. 3 for the region of the $\pi-\pi^*$ transitions, and it can be seen that it agrees rather well with experiment.

However, the TDLDA predicts 4 sharp transitions whereas experiment shows broader peaks and

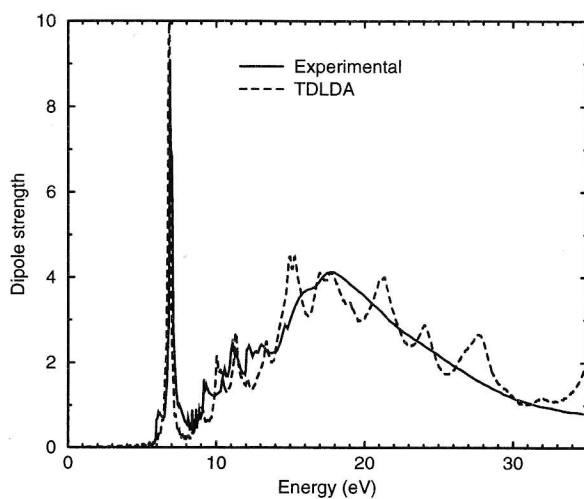


FIG. 2. Optical absorption of the benzene molecule, in units of eV^{-1} . a) experimental, from ref. [40]; b) TDLDA; [39].

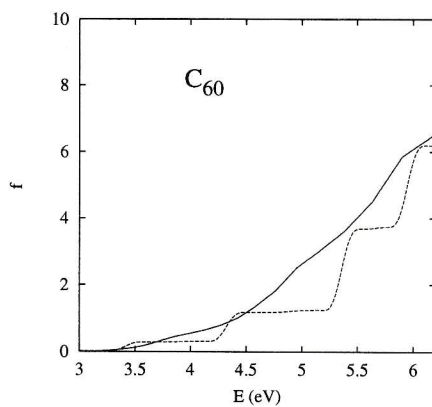


FIG. 3. Integrated strength below 6.2 eV in C_{60} , TDLDA, dashed line [39]; experiment [41], solid line.

not as many of them.

7) Demonstration that the strong, low-frequency mode in carbon chains behaves very much like the classical free-electron oscillations in a cylinder [38]. Here we found that detailed TDLDA calculations could be fit by an analytic model based on strongly collective behavior in the $\pi-\pi^*$ manifold of excitations, $\omega^2 \sim \log[L]/L$. The theoretical resonance frequencies also agreed with experiment to within 10%, for the carbon clusters that form linear chains.

8) For atoms in the IB group, we have shown that TDLDA atomic strength function calculated with the Troullier-Martins pseudopotential is nearly identical to the one calculated with all the electrons included explicitly in the range 0-50 eV [42]. This is important for the applicability of pseudopotentials to clusters of IB atoms. Doubts had been raised because the nonlocality of the pseudopotential strongly affects the TRK sum rule.

D. Work in progress

In this section, I report on work that is underway, but not yet completed. It is possible that some of it will be posted as preprints on the Los Alamos preprint server, xxx.lanl.gov, within this year.

1. Chiroptical properties by TDLDA

The above-reported calculations used only the dipole operator D , computing the correlator $\langle [D(t), D(0)] \rangle$. Another one-body operator of physical interest is the magnetic moment operator $M = e\hbar\vec{\ell}/2m$; the interference with the electric dipole gives rise to the chiroptical behavior of non-oriented molecules. Thus we can calculate these properties (circular dichroism and optical rotatory power) from the correlation function $\langle [M(t), D(0)] \rangle$. Because it is an expectation of one-body operators, we believe the mean-field approximation will be useful. Optical rotatory power and circular dichroism are the dispersive and absorptive parts of the same analytic function, and traditional methods have been inadequate for calculating the dispersive part; the only calculation in the literature of the optical rotatory power using a realistic Hamiltonian is for an exotic system

that has not even been measured [48]. Our numerical method has the advantage that there is no bias in the representation of the wave function. It automatically satisfies sum rules and produces gauge-invariant observables. In fact, the sum rule can be read out of the time-dependent response at short times. This overcomes the difficulties that more tailored bases have, that sum rules and gauge invariance may not be satisfied. We are presently calculating the molecule methyloxirane, a 10-atom molecule with known optical rotatory power in the visible and measured circular dichroism for several states in the ultraviolet [49]. For bulk systems (quartz and selenium), the TDLDA has been successful in describing the optical rotatory power [50]. In that work, it was found that the inclusion of the exchange-correlation part of the energy functional has a very large effect on the result.

2. TDLDA response of group IB elements

There are no realistic calculations of the optical response of clusters of Cu, Ag, or Au, despite the technical interest in these elemental clusters. The reason is the proximity of the d -electrons to the valence s -orbital; the d is high polarizable and strongly renormalizes the strength function. As mentioned earlier, we initially had doubts that pseudopotentials could be applied to these elements, but this was resolved satisfactorily [42]. We are therefore going ahead with calculations of small Ag and Au clusters. Numerically, the d -electrons require a fine mesh which taxes the computer resources, but clusters up to $N = 10$ are feasible. Our results will probably confirm the more schematic jellium models that predict a screening of the strong s -manifold transitions by a factor of several.

3. Ionization of Na clusters in strong fields

This project, in collaboration with an Orsay group, is stimulated by the Freiburg measurement of the competition between ionization and evaporation of Na clusters in strong fields [51]. The experiment showed that ionization of Na_{93}^+ clusters becomes probable when the laser intensity is

high enough to deposit 6-8 photons within a time of the order of 100 fs. The ionization potential is such that two photons are required to photoionize.

Our present investigation is rather schematic, because the theory of the behavior of clusters in strong fields is still not well developed, and it appears to us that models that can be easily calculated are still instructive. We are treating the electrons in a jellium model, evaluating the second-order field perturbation. However, the field contains beside the external photon an internal contribution from the surface plasmons that are excited. Since the electron interactions are all through the field, the model is in fact a simplified time-dependent mean-field theory, but in the nonlinear domain. It appears that the surface plasmons are very important for enhancing the ionization rate, not only by providing an intermediate step in the absorptive cross section, but also by dispersive field effects.

II. WHERE DO WE GO FROM HERE?

Clearly the TDLDA is a powerful theoretical tool, and we still don't know its limits of applicability. In this section we list some promising directions for the next couple of years. The common theme is to explore possible new applications of the theory.

A. Nonlinear dynamics

We believe that TDLDA is a promising theory to describe the nonlinear response of clusters to external fields, including strong fields. The single-electron dynamics is treated fully quantum mechanically, and the many-body physics is accounted for to the leading order. The weak nonlinearity, characterized by hyperpolarizabilities coefficients, has been successfully treated in the basic TDLDA approximation in both atoms [6] and clusters as large as C_{60} [54,55]. Also interesting is the ionization process. The TDLDA has already been applied to strong-field ionization in atoms [56] and small sodium clusters [57]. It is generally found that clusters are much easier to ionize than free atoms. Our schematic treatment of Na clusters verified this behavior and we would now like to apply the full TDLDA theory to sodium clusters large enough to compare with experiment

[51]. An interesting question is whether the induced fields control the physics, or whether the ionic potentials are also important.

B. Finite temperature

The TDLDA is a theory for the electronic response of a system with frozen ionic coordinates. The main new ingredient at finite temperature is that the initial state is not a single structure, but an ensemble of geometries. The response is just an ensemble average of the responses of individual structures. This neglects quantum effects in the ionic motion, but should be a reasonable approximation in many circumstances. Clearly, such problems can be treated only if there is an efficient method to generate the ensemble of states; the number of states one can contemplate including, for clusters of a few tens of atoms, is a hundred or so. A few cases that that would be interesting to study are:

- 1) Mie resonance in alkali metal clusters. The experiments of Haberland [58,59] on temperature dependence of the dipole strength function in sodium clusters shows peaks that have typical widths (FWHM) of 0.1 eV at very low temperatures, broadening to 0.5 eV temperatures above room temperature. There is already a phenomenological description of the broadening based on a random matrix Hamiltonian [60].
- 2) C₆₀. Part of the width of the UV lines is the intrinsic vibrational coupling, and part is due to the thermal excitation of C₆₀. Spectra have been measured at 800K and cold in solution, and some broadening is seen.
- 3) Opacity of dense plasma. This is beyond the scope of this proposal, but should be mentioned in the catalog of possible TDLDA applications. Currently, the state of the art in calculating the optical absorption in dense plasmas is to use static mean field theory with an LDA energy functional, or a CI expansion [61]. The low-frequency oscillator strength is of course strongly affected by the interaction, and the TDLDA extension would be very natural. The opacity of rare gas clusters at densities around 1 gm/cm³ and temperature around 10 eV is very relevant to the phenomenon of sonoluminescence, according to the theory of Moss et al. [62].

C. Electron-vibration coupling

The electron-vibration coupling is important for many physical processes: the infrared oscillator strength, resistivity and superconductivity in bulk systems, and the damping of oscillator strength in larger molecules. In early studies we investigated this coupling using simplified tight-binding models of the electron wave function, but a calculation of the infrared strength in C_{60} showed that such models are quite unreliable [66]. In contrast, the LDA seems to work up to a factor of two or better. In an older study using a different algorithm [67], we investigated the coupling of the collective dipole mode in Na clusters to vibrations. While TDLDA worked well for Na_2 , we were not successful in Na_8 . The algorithm was not fast enough to treat all of the vibration couplings, and the mode that we did treat had only a fraction of the needed strength. We would like to revisit this question with our much faster algorithm. We are interested only in the width of the absorption strength, so the vibrational degrees of freedom can be treated semiclassically. A goal farther down the road is to understand the widths of the strong transitions in C_{60} in the ultraviolet. There are approximately four peaks, each with a width of about 0.3 eV (FWHM). Also in C_{60} : the absorption in the green, due to vibronic coupling to forbidden transitions, has yet to be explained from *ab initio* theory. Since these are weak transitions, it is less clear that the TDLDA will have a useful accuracy (factor of two or better).

D. Better energy functionals

Our view up to now is to take a well-documented LDA functional and investigate the full range of predictions. However, it is clear that when one considers systems with unpaired electrons, the generalization to a functional of local spin density is very natural. With another collaborator, Susumu Saito, Yabana and I plan to investigate systems where the spin might be significant. One possibility is small aluminum clusters. Al_2 is known to have a triplet ground state; its optical absorption cross section might be sensitive to the treatment of spin in the energy functional.

Recently a gradient-corrected energy functional has been found, the so-called GGA, that significantly improves the agreement for ground state energies [31] as well as excitation energies

in simple molecules [16]. If its success continues, we will eventually want to use it in the TDLDA calculations. However, at present the continuation of the systematic survey with the simpler functional has higher priority.

The pseudopotential prescription we use is susceptible to the appearance of ghost states for certain choices of the angular momentum channels to be treated nonlocally. Recently, Goedecker and collaborators [63] have proposed ghost-free pseudopotentials (based on Gaussians) that are smoother than previous ones. With a smoother potential, it may be possible to use a coarser mesh, which would be very helpful for the computational effect.

E. Algorithmic improvements

Our representation for the wave function, a three-dimensional spatial lattice, requires large vectors and very intensive computing, typically using supercomputers or the latest generation of work stations. Small improvements in the lattice representation could have large benefits because the vector size varies as the cube of the one-dimensional mesh. We would like to investigate nonuniform meshes, with closer spacing in regions where the electron kinetic energy is high. We believe that approaches subdividing initially uniform meshes may be promising; another approach uses a coordinate transformation to shrink and expand the mesh in different regions [64].

Another area of possible algorithmic improvement is to use the Hamiltonian operator in a different way. In the real-time method, the basic calculation is of the operator $e^{-i \int H dt}$ acting on the initial wave function. This typically requires 10^4 applications of H to a vector to approximate the wanted operator multiplication. There might be some completely different technique that would require far fewer Hamiltonian-on-vector multiplications. For example, the Lanczos algorithm can be generalized to the RPA Hamiltonian matrix. Each $H\Psi$ multiplication gives data for a discrete approximation to the strength function that satisfies one additional moment of the Hamiltonian [65]. If this can be applied to the TDLDA Hamiltonian, the computation time could be reduced by an order of magnitude or more, and the method could be routinely applied.

If the response is only desired at a specific frequency, a good technique is to solve the Green's

function as in the Sternheimer method. This has been successfully applied to atoms, solving the equation iteratively [8]. Specifically, one can apply the conjugate gradient method with a double loop on the the wave function optimization and the self-consistent field optimization.

III. ACKNOWLEDGMENT

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