

Pseudojellium model with an application to lithium clusters

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Ionic pseudo-Hamiltonians, which replace core electrons in atomic calculations, are used to build a jelliumlike model, which describes electronic ground state and excitation properties of atomic clusters. As an application, we successfully describe the plasmon resonance in lithium clusters for which recent experimental data have shown the failure of the conventional jellium model.

Self-consistent calculations¹⁻³ of ground-state properties and excited states of small metal particles, within the local-density approximation (LDA) applied to the jellium model (JM), have become of common use in the past few years. Despite its simplicity, this approach has provided a good description of the optical properties of some alkali metal clusters, namely, those made of Na and K atoms. In particular, the collective plasmon resonances in these clusters, whose existence is well established experimentally,^{4,5} have been interpreted within the random-phase approximation as coherent electron-hole excitations.

Very recently, Bréchnignac *et al.*⁶ have reported measurements of the photoabsorption cross section of Li cluster ions and have pointed out the difficulty to interpret them within the JM. Motivated by these results, we present in this work a new model of atomic clusters. We call it the pseudojellium model (PJM) because, compared to the conventional JM, it adopts a more accurate description of the electron-ion interactions (the pseudo-Hamiltonian), yet it keeps the conceptual simplicity of the JM and thus allows the self-consistent calculation of ground-state properties and excitation spectra of very large clusters. In what follows we first describe our model and then show that, unlike the conventional JM, it explains the optical properties of singly ionized Li clusters.

Calculations of cluster properties are often based on the following electronic energy functional:

$$E = E_{\text{kin}} + E_{\text{xc}} + E_{\text{es}} + E_{\text{ei}}, \quad (1)$$

where E_{kin} , E_{xc} , E_{es} , and E_{ei} are, respectively, the kinetic, exchange-correlation, electrostatic, and electron-ion parts of the total energy of the system of N valence electrons. The electrostatic part E_{es} is given by (atomic units are used throughout this paper, except otherwise stated)

$$E_{\text{es}}(\rho) = \frac{1}{2} \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}', \quad (2)$$

where $\rho(\mathbf{r})$ is the density of valence electrons. In the JM one approximates the real distribution of positive ions by a model ionic density which is constant inside a sphere of radius R and zero outside it

$$n^+(\mathbf{r}) = n_0 \Theta(R - r), \quad (3)$$

i.e., a spherical step density whose parameters n_0 and R are related to the Wigner-Seitz radius r_s , the number of atoms in the cluster Z , and of valence electrons of each atom z_v [$n_0 = 3/4\pi r_s^3$; $R = r_s(z_v Z)^{1/3}$], and then assumes that the electron-ion interaction is simply described by the electrostatic potential due to such a model ionic density

$$V_I(\mathbf{r}) = - \int \frac{n^+(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \quad (4)$$

The corresponding electron-ion energy term in Eq. (1) is

$$E_{\text{ei}} = \int \rho(\mathbf{r}) V_I(\mathbf{r}) d\mathbf{r}. \quad (5)$$

The assumption (4) is very crude and takes no account of the structure of the ions. It evidently amounts to a point-charge approximation of the ionic potential, which cannot resolve any chemical difference between, say, two isovalent ions belonging to the same group of the periodic table. In fact, some of the failures of the JM in describing correctly the plasmon energies in metal clusters such as Li clusters⁶ point to this inadequacy of Eq. (4).

It has been shown that the electron-ion interaction can be represented in a more realistic way by angular momentum-dependent pseudopotentials⁷ or alternatively by velocity-dependent pseudo-Hamiltonians.⁸ In this work we generalize the JM by substituting the as-

sumption (4) with the following one:

$$\hat{V}_I = \int n^+(\mathbf{r}') h(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (6)$$

i.e., the ions are still being spherically averaged using the model ionic density n^+ of Eq. (3) (jellium approximation) but, instead of describing the ion-electron interaction by $-1/|\mathbf{r} - \mathbf{r}'|$, it is now represented by the pseudo-Hamiltonian⁸

$$h(|\mathbf{r} - \mathbf{r}'|) = -\frac{1}{2} \nabla_{\mathbf{r}-\mathbf{r}'} a(|\mathbf{r} - \mathbf{r}'|) \cdot \nabla_{\mathbf{r}-\mathbf{r}'} + \frac{1}{2} \mathbf{L}_{\mathbf{r}-\mathbf{r}'} \frac{b(|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|^2} \cdot \mathbf{L}_{\mathbf{r}-\mathbf{r}'} + v(|\mathbf{r} - \mathbf{r}'|), \quad (7)$$

which describes the relative motion of an electron with coordinate \mathbf{r} and an ion at point \mathbf{r}' . We shall therefore refer to it as the PJM. In Eq. (7), a , b , v are radial functions and $\mathbf{L}_{\mathbf{r}-\mathbf{r}'}$ is the angular momentum operator with respect to the position \mathbf{r}' . Outside the core of an atom, a and b vanish and $v = -1/|\mathbf{r} - \mathbf{r}'|$. Inside the core the radial functions a , b and v are determined to optimally replace a full core atom with a pseudo- (valence only) atom.⁸ They are shown in Fig. 1 for the case of the Li atom. From Eqs. (6) and (7) by integrating over \mathbf{r}'

$$\left(-\frac{1}{2} \nabla [1 + \alpha(r)] \cdot \nabla + \mathbf{L}\beta(r) \cdot \mathbf{L} + u(r) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta E_{xc}(\rho)}{\delta \rho} \right) \varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}). \quad (11)$$

Note that, since the potential \hat{V}_I has the important property of being momentum and angular-momentum dependent, the Kohn-Sham equations have a modified kinetic energy operator which, just like the case of an isolated ion, can be interpreted in terms of a radial- and direction-dependent effective mass tensor.⁸ Notice, however, that the global radial term α [Eqs. (8) and (11)] or in other words the radial effective mass $m^*(r) = 1/[1 + \alpha(r)]$ is

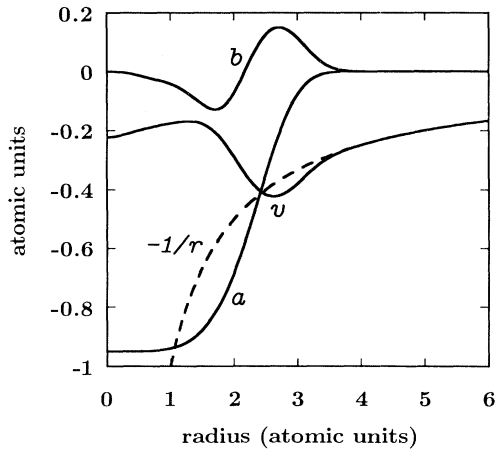


FIG. 1. The radial kinetic energy factors, $a(r)$ and $b(r)$, and the atomic potential, $v(r)$ of Eq. (7), for the lithium atom in atomic units.

one gets

$$\hat{V}_I(r) = -\frac{1}{2} \nabla \alpha(r) \cdot \nabla + \mathbf{L}\beta(r) \cdot \mathbf{L} + u(r), \quad (8)$$

where $\alpha(r) = A_0^{(2)}(r) + \frac{4}{3} B_0^{(4)}(r) - \frac{4}{3} B_2^{(4)}(r)$, $\beta(r) = B_0^{(2)}(r) - \frac{2}{r} B_1^{(3)}(r) + \frac{1}{r^2} B_2^{(4)}(r)$ and $u(r) = V_0^{(2)}(r)$, with

$$\begin{aligned} A_0^{(2)}(r) &= \int r'^2 n^+(r') a_0(r, r') dr', \\ V_0^{(2)}(r) &= \int r'^2 n^+(r') v_0(r, r') dr', \\ B_L^{(k)}(r) &= \int r'^k n^+(r') \tilde{b}_L(r, r') dr'. \end{aligned} \quad (9)$$

In Eq. (9), the quantities $a_L(r, r')$, $v_L(r, r')$, and $\tilde{b}_L(r, r')$ are the coefficients of the multipole expansions of $a(|\mathbf{r} - \mathbf{r}'|)$, $v(|\mathbf{r} - \mathbf{r}'|)$ and $b(|\mathbf{r} - \mathbf{r}'|)/2|\mathbf{r} - \mathbf{r}'|^2$, respectively.

With the introduction of the pseudo-Hamiltonian, the electron-ion energy becomes

$$E_{ei} = \sum_{i(\text{occ})} \int \varphi_i^*(\mathbf{r}) \hat{V}_I \varphi_i(\mathbf{r}) d\mathbf{r}, \quad (10)$$

where the φ_i are the self-consistent solutions of the Kohn-Sham equations for the spherical PJM

built up from both radial and angular terms of the individual ion [Eq. (9)]. The presence of a modified mass also has the effect of changing the integrated oscillator strength $m_1 \equiv \sum_n \omega_n |\langle 0|D|n \rangle|^2$ of the dipole operator $D = \sum_{i=1}^N z_i$

$$m_1^{\text{PJM}} = \frac{1}{2} \int [1 + \alpha(r) + \frac{4}{3} r^2 \beta(r)] \rho(r) dr \equiv \frac{N_{\text{eff}}}{2} \quad (12)$$

as compared to the JM result

$$m_1^{\text{JM}} = \frac{N}{2}. \quad (13)$$

In Fig. 2 we have plotted, for the example of a Li_{20} cluster, the radial effective mass $m^*(r)$ as a function of the distance from the center of the cluster. We see that a more realistic description of the electron-ion interaction based on ionic pseudo-Hamiltonians gives, for a jellium cluster of Li atoms, a considerable increase of the electronic effective mass inside the cluster volume. We have also evaluated in Li_{20} the effective number N_{eff} of valence electrons defined by Eq. (12), finding $N_{\text{eff}}=15$. One can thus interpret the effect of a realistic electron-ion interaction on the dipole excitation as a reduction of the number of valence electrons involved in the collective motion.

As a testing ground of the PJM we choose to apply it to the case of singly ionized Li clusters, where recent experimental data⁶ have shown the deficiency of the JM. Starting from the energy functional we have

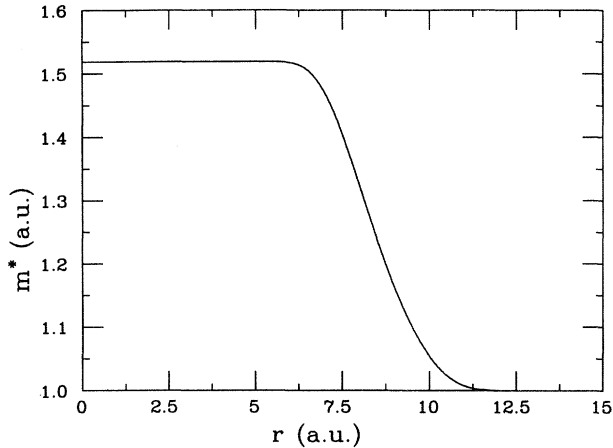


FIG. 2. Effective mass m^* calculated in Li_{20} .

solved the Kohn-Sham equations (11) with $r_s=3.26$ a.u., and calculated the dipole response functions in the time-dependent LDA (TDLDA).⁹ The simple structure of the energy functional makes it possible to reduce the TDLDA problem to a one-dimensional integral equation in coordinate space. In practice, this is solved by using an integration step of 0.2 a.u. for all systems considered here. We have calculated the dipole strength functions $S(\omega) = \sum_n |\langle n|D|0\rangle|^2 \delta(\omega - \omega_{no})$ where $|n\rangle$ and ω_{no} are the excited states and corresponding excitation energies. To make the analysis of $S(\omega)$ easier, the δ peaks have

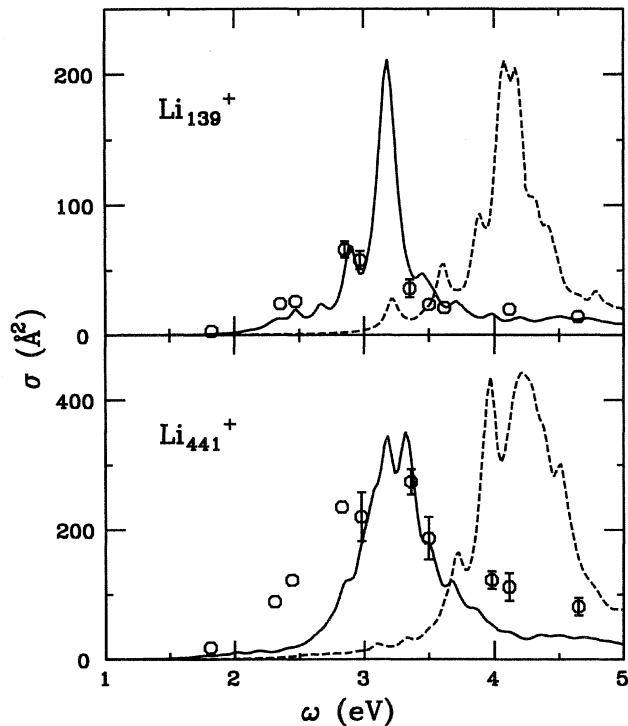


FIG. 3. Calculated RPA dipole photoabsorption cross sections of Li_{139}^+ and Li_{441}^+ clusters. Solid and dashed curves correspond to PJM and JM calculations, respectively. Experiments are from Ref. 6.

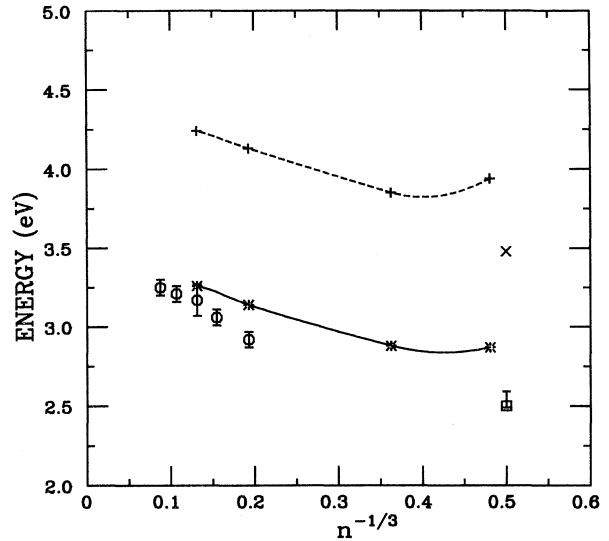


FIG. 4. Evolution with size of the peak energy of the plasmon resonance for Li clusters. Experimental points for ionized clusters (open circles with bars) are from Ref. 6 and for neutral Li_8 (vertical bar) is from Ref. 10. Crosses and stars correspond to the JM and PJM results for ionized clusters, respectively. Calculated results in Li_8 are also shown by a diagonal cross (JM) and square (PJM).

been folded with Lorentzian curves of width $\Gamma=110$ meV.

In Fig. 3 are shown the calculated photoabsorption cross sections $\sigma(\omega) = [4\pi^2\omega/c]S(\omega)$ in JM and PJM. The calculation fulfills the integrated oscillator strength m_1 [Eqs. (12) and (13)] within $\approx 2\%$. The striking feature is the large shift between the two models. Part of this shift can be attributed to the larger single-particle level density of the PJM due to its larger effective mass. The general shape of the distributions is not much changed in the two models. On the same figure are reported the corresponding data of Ref. 6. Although there is some uncertainty in the absolute magnitude of measured cross sections, the peak energies are certainly well determined. Figure 3 shows a good agreement of the experimental peaks with PJM results whereas the JM predictions are off by about 1 eV. In Fig. 4 we compare the JM and PJM calculated peak energies for Li cluster ions ranging from Li_9^+ ($N=8$) to Li_{441}^+ ($N=440$), together with measured peak energies taken from Ref. 6 ($N \geq 139$). On the same figure are shown calculated values for the neutral cluster Li_8 which has been also measured.¹⁰ The PJM energies are systematically lower than the JM ones by about 1 eV, resulting in a remarkable agreement with experiment.

In conclusion, we have shown the importance of the effects of core electrons on valence electrons in atomic clusters of the Li type. These effects can be treated by means of pseudo-Hamiltonians. The resulting pseudojellium model keeps the conceptual simplicity of the usual jellium model and leads to a quantitative understanding of optical properties of a wide range of Li cluster ions.

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deed be less good than state-of-the-art pseudopotentials), but instead, we address eV-sized absorption peak shifts between the jellium model and the experimental data of lithium clusters. To describe lithium ions on this energy scale many reasonable pseudo-Hamiltonians and pseudopotentials are equally good, as long as they contain the physics which makes the lithium ion essentially different from heavier alkali ions. This physics amounts to a strong angular-momentum dependence of the electron-ion interaction, due to the fact that *s*-like valence electrons are pushed away from the nucleus by the presence of an *s*-like core, while *p*-like valence electrons have no underlying *p*-like core in lithium and are, thus, not repelled. This physics is adequately described by the pseudo-Hamiltonian adopted in our work (Fig. 1), as many atomic tests suggest.

⁹This approximation is sometimes called RPA in other fields, e.g., in nuclear physics, see, for example, G.F. Bertsch and S.F. Tsai, Phys. Rep. **18C**, 126 (1975).

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