

Alkali-metal plasmons, pseudopotentials, and optical sum rules

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Starting from recent experimental and theoretical results on the optical absorption of lithium clusters, we reexamine some effects of the angular-momentum dependence of the electron-ion interaction, a necessary ingredient of accurate valence-only atoms. Our theoretical results are compared to a variety of optical data for alkali-metal atoms, clusters, and bulk solids, and illustrate interesting aspects of the jellium approximation and of optical sum rules, when based on first-principles pseudopotentials. [S0163-1829(97)06619-8]

I. INTRODUCTION

In a recent series of papers Serra and co-workers¹⁻³ have introduced a simple model for the optical properties of alkali-metal clusters, the pseudojellium model (PJM). In this model an angular-momentum-dependent electron-ion interaction is taken into account only through its spatial average over a sphere. In the first paper¹ a local pseudo-Hamiltonian⁴ was adopted. As a result the main peak of the photoabsorption cross section of Li clusters (known as Mie resonance in a classical context⁵) was found to be redshifted by about 1 eV with respect to the predictions of the conventional JM (jellium model⁶). This model provided a qualitative explanation of the photoabsorption experiments of Brechignac *et al.* on Li clusters,⁷ and at first sight even a fairly good quantitative explanation. The redshift of the Mie resonance energy in Li was then attributed to the angular-momentum dependence of the electron-ion interaction, whose consequences survive even after a spatial average. The result of the PJM for Li clusters was understood in terms of a greatly enhanced effective mass (up to 50% near the center of all clusters) and gave a modified sum rule for the oscillator strengths which also seemed to match the experimental findings. In two subsequent papers^{2,3} the PJM was used in connection with nonlocal pseudopotentials rather than pseudo-Hamiltonians for the evaluation of bulk and cluster properties of alkali metals. This work, prompted by a model calculation by Yabana and Bertsch,⁸ allowed a more accurate estimate of the nonlocal contribution, but confirmed the validity of the original qualitative explanation of the redshift. Finally, recent self-consistent calculations of the optical properties of very small lithium clusters, also based on nonlocal pseudopotentials, accurately reproduced the experimental red shift but apparently overlooked the simple physical interpretation (the strong ionic nonlocality) which makes the optical response of lithium clusters so different from jellium spheres and from the other alkali-metal clusters.⁹ These results give us the mo-

tivation for a closer look at some nontrivial properties of nonlocal electron-ion interactions which are not peculiar to clusters, and to put them together with a variety of optical data for alkali metals, and for Li in particular. The purpose is a deeper understanding of the experiments on clusters but also, more generally, of the jellium approximation and of optical sum rules when used in connection with first-principles nonlocal pseudopotentials. One of the conclusions of this paper is in fact that sum rules, often used for model metallic clusters (see, e.g., Refs. 2 and 3, and references therein), should be handled with some care whenever valence-only systems are considered. In what follows, we will mostly deal with either bulk (jellium) solids or isolated atoms, keeping in mind the existing results for clusters. In bulk Li a large shift of the plasmon peak with respect to the jellium predictions was suggested by various measurements (electron-energy-loss spectroscopy,¹⁰ EELS) optical properties^{11,12}), but the exact magnitude of this shift was not well established, ranging from 0.9 to 1.3 eV. In the past this shift was generically attributed¹³ to the particularly strong electron-ion interaction of lithium, but the key role of its angular-momentum dependence, or nonlocality, had never been recognized. Only recently Serra *et al.*¹ emphasized this role for clusters, and shortly after Yabana and Bertsch⁸ specified the amount of the nonlocal contribution using an empirically adjustable model pseudopotential. Here we see in detail how the average nonlocality [which survives in the PJM (Ref. 1)] contributes to the red shift, and show that it can be accurately estimated from first-principles pseudopotentials. The physics behind modified optical sum rules for valence electrons is also reexamined. On this issue many ingredients were available in the literature: the Fano-Cooper theory on the core-valence transfer of oscillator strength,¹⁴ the relation between general nonlocal potentials and optical sum rules,¹⁵ and the calculation of a few oscillator strengths for selected valence-only systems;¹⁶ but to our knowledge the connection among these three ingredients, and thus a consistent physical interpretation of the meaning and reliability of modified sum rules ob-

tained from first-principles pseudopotentials, was still lacking.

II. JELLIUM IONS AND PSEUDOIONS

Nonlocal pseudopotentials can always be split into a local part with a long-range Coulomb tail and a short-range non-local part, whose spatial extent is of the order of the atomic core:

$$\hat{v}^{\text{PS}} = \hat{v}_{\text{loc}} + \Delta\hat{v}. \quad (1)$$

The kernel of $\Delta\hat{v}$, in the coordinate representation, is

$$\Delta v(\mathbf{r}, \mathbf{r}') = \frac{\delta(r-r')}{rr'} \sum_{\ell=0}^{\ell_{\text{max}}} \sum_{m=-\ell}^{\ell} Y_{\ell m}(\hat{\mathbf{r}}) Y_{\ell m}^*(\hat{\mathbf{r}}') \Delta v_{\ell}(r), \quad (2)$$

while the kernel of the local part is simply given by $\delta(\mathbf{r}-\mathbf{r}')v_{\text{loc}}(\mathbf{r})$. In a true Li crystal the potential felt by the valence electrons is given by a sum of ionic pseudopotentials centered at the bcc lattice sites \mathbf{R} ; in the PJM a shapeless background, obtained as a spatial average, replaces the true, discrete lattice of ions. Because of the Coulomb tail the local part averages to

$$\bar{v}_{\text{loc}}(\mathbf{r}) = \lim_{V \rightarrow \infty} \frac{N}{V} \int_V d^3R v_{\text{loc}}(\mathbf{r}-\mathbf{R}) = \lim_{k \rightarrow 0} \left[-\frac{4\pi}{k^2} \frac{1}{\Omega_c} + \alpha \right], \quad (3)$$

where Ω_c is the volume of the unit cell of the crystal and α is a constant; the divergent term is later balanced by the divergence of the electrostatic potential of the valence electrons (the Hartree term), since the unit cell is electrically neutral. The spatial average of the nonlocal kernel $\Delta v(\mathbf{r}, \mathbf{r}')$ gives, in turn,

$$\begin{aligned} \Delta \bar{v}(\mathbf{r}, \mathbf{r}') &= \lim_{V \rightarrow \infty} \frac{N}{V} \int_V d^3R \Delta v(\mathbf{r}-\mathbf{R}, \mathbf{r}'-\mathbf{R}) \\ &= \int \frac{d^3k}{(2\pi)^3} e^{i\mathbf{k} \cdot (\mathbf{r}-\mathbf{r}')} f^{\text{PP}}(k); \end{aligned} \quad (4)$$

$$f^{\text{PP}}(k) = \frac{4\pi}{\Omega_c} \sum_{\ell=0}^{\ell_{\text{max}}} (2\ell+1) \int_0^{\infty} dr r^2 [j_{\ell}(kr)]^2 \Delta v_{\ell}(r) \quad (5)$$

is the Fourier transform $\int d^3r d^3r' e^{-i\mathbf{k} \cdot \mathbf{r}} \Delta v(\mathbf{r}, \mathbf{r}') e^{i\mathbf{k}' \cdot \mathbf{r}'}$, calculated for $\mathbf{k}' = \mathbf{k}$. It depends on the modulus k because ions are spherically symmetric. The average nonlocal potential, whose kernel is $\Delta \bar{v}(\mathbf{r}, \mathbf{r}')$, has full translational and rotational invariance, its eigenfunctions are plane waves $e^{-i\mathbf{k} \cdot \mathbf{r}}$, and the corresponding eigenvalues evidently introduce an additional k dependence

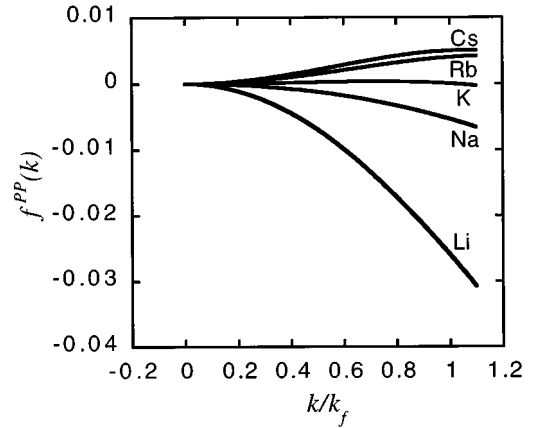


FIG. 1. Fourier transform of the nonlocal correction $f^{\text{PP}}(k)$ [Eq. (5)] for alkali ions with pseudopotentials of Ref. 18, and $\ell_{\text{max}}=2$. The curves are aligned to a common zero.

$$\epsilon_{\mathbf{k}}^{\text{PP}} = \frac{k^2}{2} + f^{\text{PP}}(k), \quad (6)$$

to the single-particle energies, which obviously modifies the effective mass. In the absence of nonlocal effects, instead, the correction to the free-electron dispersion relation would amount to a k -independent constant shift, which does not alter the slope and curvature of $\epsilon_{\mathbf{k}}$ and thus leaves unchanged the effective mass.¹⁷ $f^{\text{PP}}(k)$ has been calculated for k ranging from 0 to k_F for all alkali metals using s , p , and d pseudopotentials,¹⁸ i.e., using $\ell_{\text{max}}=2$ in Eq. (5). The results, after lining them up at $k=0$, are shown in Fig. 1. The curves are aligned to a common zero because we are ultimately interested in effective masses. We see that $f^{\text{PP}}(k)$ shows the strongest k dependence for Li, which we immediately understand in terms of its much stronger s - p nonlocality: compared to the other alkali-metal atoms, the Li ionic core contains s electrons but no p electrons. The splitting of \hat{v}^{PS} into a long-range local part \hat{v}_{loc} and a short-range nonlocal correction $\Delta\hat{v}$ [Eq. (1)] is of course not unique, since, if consistently performed, it simply amounts to adding a short-range, ℓ -independent correction $w(r)$ to all the angular-momentum radial components $\Delta v_{\ell}(r), \ell=0 \dots \infty$, of Eqs. (2) and (5), and to subtracting the same $w(r)$ from the local potential of Eqs. (1) and (3). However, we immediately see that the Fourier components of the total potential, as well as the k dependence of f^{PP} , are independent of the particular choice of the local potential.¹⁹ Even if, as usually done for practical reasons, the choice of the local potential is not fully consistent (the above sums do not include all the terms $\ell=0 \dots \infty$, but only up to ℓ_{max}), the k dependence of f^{PP} , as we numerically checked, is only marginally affected, provided that ℓ_{max} is sufficiently high and the choice of the local, long-range Coulomb part is physically sensible (which is the general rule for any solid-state or molecular application of ionic nonlocal pseudopotentials). Such a small effect of the truncation of the ℓ sums can also be understood from a simple power expansion around $k=0$:

$$\begin{aligned}
\frac{\Omega_c}{4\pi} f^{\text{PP}}(k) &= \int r^2 dr \Delta v_0(r) + \frac{k^2}{3} \int r^4 dr [\Delta v_1(r) - \Delta v_0(r)] \\
&+ \frac{k^4}{45} \int r^6 dr \{-2[\Delta v_1(r) - \Delta v_0(r)] \\
&+ [\Delta v_2(r) - \Delta v_1(r)]\} + \frac{k^6}{1575} \int r^8 dr \\
&\times \{5[\Delta v_1(r) - \Delta v_0(r)] - 4[\Delta v_2(r) - \Delta v_1(r)] \\
&+ [\Delta v_3(r) - \Delta v_2(r)]\} + \dots,
\end{aligned}$$

which shows that the absence of higher- ℓ components only affects the higher powers of k in the expansion. A k -dependent correction to the single-particle eigenvalues is also obtained when, rather than pseudopotentials, the electron-ion interaction is represented by ionic pseudo-Hamiltonians,⁴ but in this case the correction turns out to be purely quadratic:

$$\begin{aligned}
\hat{h}_{\mathbf{r}} &= -\frac{1}{2} \nabla_{\mathbf{r}} a(r) \nabla_{\mathbf{r}} + \frac{b(r)}{2r^2} \mathbf{L}_{\mathbf{r}}^2 + v(r), \\
\frac{\Omega_c}{4\pi} f^{\text{PH}}(k) &= \frac{k^2}{2} \int dr r^2 a(r) + \left\{ \frac{1}{2} \sum_{\ell} \ell(\ell+1)(2\ell+1) \right. \\
&\times \left. \int_0^{\infty} dr [j_{\ell}(kr)]^2 b(r) \right\} \quad (7) \\
&= k^2 \left[\frac{1}{2} \int dr r^2 a(r) + \frac{1}{3} \int dr r^2 b(r) \right],
\end{aligned}$$

which also implies that the pseudo-Hamiltonians will reasonably track the pseudopotentials only up to some finite k .^{20,21} Now we can put together experiments and jellium theories for cluster and bulk metals. The random-phase approximation predicts

$$\omega_p^2 = \frac{4\pi n e^2}{m_{\text{opt}}};$$

the key quantity for the energy location of the plasmon peak is the optical effective mass, which, for an isotropic Fermi surface, is given by

$$m_{\text{opt}} = \left[\frac{1}{k} \frac{\partial \epsilon_{\mathbf{k}}}{\partial k} \right]_{k=k_F}^{-1}.$$

Collective excitations of surfaces and clusters are then

$$\omega_p = \omega_s \sqrt{2} = \omega_M \sqrt{3},$$

where ω_s is the frequency of the surface plasmon,²² and the last equation should hold for jelliumlike models of very large clusters.⁶ The PJM based on pseudo-Hamiltonians [Eq. (7)] gives, for bulk Li, an optical effective mass $m_{\text{opt}}^{\text{PH}} = 1.53$, which agrees with the corresponding results of Serra *et al.* for large clusters.¹ On the other hand, using (more accurate) nonlocal pseudopotentials we obtain $m_{\text{opt}}^{\text{PP}} = 1.15$, substantially smaller than 1.5, but still larger than the plain jellium model ($m_{\text{opt}}^{\text{JM}} = 1$ for all the alkali metals). This confirms that for Li clusters the use of pseudo-Hamiltonians¹ gave the

TABLE I. Plasma frequency (in eV) of alkali metals in various models and from experiments: for the plain JM, using the electronic densities of Ref. 23, we show it ‘‘as it is’’ in the first column ($\hbar\omega_p$) and divided by the square root of the core polarizability ($\hbar\bar{\omega}_p$) in the second column. Experimental values (third column) are taken from Refs. 10 and 11 (lithium) and Ref. 24 (Na–Cs). The fourth and fifth column show the plasma energy divided by the square root of the core polarizability for the PJM based on nonlocal pseudopotentials and pseudo-Hamiltonians.

Elem.	$\hbar\omega_p^{\text{JM}}$	$\hbar\bar{\omega}_p^{\text{JM}}$	$\hbar\omega_p^{\text{exp}}$	$\hbar\bar{\omega}_p^{\text{PP}}$	$\hbar\bar{\omega}_p^{\text{PH}}$
Li	8.04	7.97	7.12	7.42	6.45
Na	6.04	5.84	5.72	5.71	5.73
K	4.40	4.06	3.72	4.03	4.09
Rb	3.97	3.53	3.41	3.57	3.69
Cs	3.54	3.08	2.99	3.11	3.29

right qualitative explanation but too large an effect, as initially pointed out by Yabana and Bertsch⁸ and later confirmed by Alasia *et al.*,³ here we add that the main reason of such an overshooting is a mediocre transferability of first-row pseudo-Hamiltonians.²¹ In summary, for bulk Li the angular-momentum dependence of the electron-ion interaction, when accurately described, is sufficient to explain only part of the shift of the plasmon peak with respect to the plain jellium model: even the smallest experimental estimate, based on EELS,¹⁰ corresponds to an effective mass of 1.27, which is larger than 1.15. For alkali metals other than Li, instead, pseudopotentials agree with pseudo-Hamiltonians, and both predict only a small correction to the jellium model. This also gives a reasonable agreement with experiments after including a core-polarizability correction (an effect which can be significant for ‘‘fat’’ cores but is very small for Li), as shown by Tables I and II. The result obtained here with first-principles pseudopotentials matches the semiempirical estimate by Yabana and Bertsch,⁸ who deduced the nonlocal contribution to the effective mass from the comparison of the experimental value of the optical effective mass and the theoretical effective mass based on local Li pseudopotentials. It also agrees with the large-cluster limit³ and bulk estimates² of Lipparini and co-workers. A lattice of local potentials opens energy gaps at the Bragg planes, but, also, to a lesser extent, it modifies the energy-versus-wave-vector dispersion everywhere in the Brillouin zone, and thus it also makes a contribution to the effective mass, which, unlike the nonlocal contribution, does not survive in any jellium approximation. In conclusion, both nonlocality and the discrete spatial arrangement of ions affect the electronic effective mass; the

TABLE II. Optical effective masses for the alkali metals in the PJM with pseudopotentials and pseudo-Hamiltonians.

Elem.	$m_{\text{opt}}^{\text{PP}}$ PJM	$m_{\text{opt}}^{\text{PH}}$ PJM
Li	1.153	1.526
Na	1.049	1.040
K	1.014	0.983
Rb	0.977	0.909
Cs	0.983	0.872

nonlocal contribution is particularly relevant for lithium, and norm-conserving pseudopotentials give an accurate first-principle estimate thereof.²⁵

III. SUM RULES AND PSEUDOIONS

The nonlocality of the electron-ion interaction has another consequence on the optical photoabsorption of an electronic system, namely, the violation of the f -sum rule, which for condensed systems is the same as the Thomas-Reiche-Kuhn sum rule for atomic oscillator strengths.²⁶ The issue is of interest because both experiments⁷ and theory¹ initially suggested a violation of this rule for Li clusters. As is known, the optical sum rule relates the value of the integrated photoabsorption cross section $\sigma(\omega)$ of an optically excited electronic system to the total number of electrons in the system N ; in other words, the sum of the oscillator strengths f_{0k} for optical transitions from the initial state 0 to any allowed final state k (hence the name “ f sum”) adds up to $N/2$. In the framework of first-order perturbation theory, with the electromagnetic field treated as a small perturbation applied to a system of N interacting electrons, the f -sum rule reads:

$$f = \int d\omega \sigma(\omega) = \sum_k f_{0k} = \sum_k (E_k - E_0) |\langle \Psi_0 | \mathbf{D} | \Psi_k \rangle|^2 = \frac{N}{2}, \quad (8)$$

the sum being extended over the whole energy spectrum of the electronic excitations; here \mathbf{D} is the dipole operator, the many-electron quantum states $|\Psi_k\rangle$ form a complete and orthonormal set of eigenstates of the unperturbed Hamiltonian \hat{H}_0 , and E_k are the corresponding energies. The sum over the excited states $|\Psi_k\rangle$ can be written as the ground-state expectation value of the double commutator between the Hamiltonian $\hat{H}_0 = \hat{T} + \hat{V}$ and the dipole operator \mathbf{D} . If we have a standard local potential \hat{V} (i.e., simply multiplicative), Eq. (8) follows immediately. On the other hand, as soon as an explicit dependence on the electronic angular momentum appears in the Hamiltonian, as with nonlocal pseudopotentials \hat{v}^{ps} (Eq. 1), or pseudo-Hamiltonians \hat{h}_r [Eq. (7)], additional terms appear in the commutator, which result in a modified f sum.²⁷ We have evaluated the f sum for each alkali-metal *pseudoatom* ($N = N_v = 1$), and compared it with the corresponding valence-only sum for the true, full-core atom, obtained from available experimental data; this helps us to understand whether the modification of the standard f -sum rule introduced by pseudopotentials reflects some physical property of the valence electrons of true atoms, or is an unwanted consequence of a mathematical trick to be aware of; it will in particular shed some light on experimental and theoretical f sums for Li clusters.^{7,1} If we adopt s - p nonlocal potentials to describe the electron-ion interaction [i.e., $\ell_{\max} = 1$ in Eq. (2)], for $N^{\text{PP}} = 2f$ we obtain

$$N^{\text{PP}} = 1 + \frac{2}{3} \int dr r^4 R_{1s}^2(r) [\Delta v_p(r) - \Delta v_s(r)], \quad (9)$$

where R_{1s} is the one-electron radial wave function of the ground-state pseudoatom; we see that nonlocality, i.e., the

TABLE III. Modified f -sum rule: results obtained with nonlocal pseudopotentials (first column), and with pseudo-Hamiltonians (second column). In the last two columns are instead shown the sum of oscillator strengths restricted to the discrete spectrum for nonlocal pseudopotentials (third column) and experiments (fourth column, from Ref. 28).

Elem.	N^{PH}	N^{PP}	N_d^{PP}	N_d^{exp}
Li	0.97	0.93	0.70	0.75
Na	1.00	1.00	0.93	0.97
K	1.03	1.04	1.00	1.01
Rb	1.10	1.10	1.08	1.09
Cs	1.16	1.16	1.13	1.19

difference between the potential “felt” by s and p electrons, modifies the sum rule with respect to the actual number of valence electrons which is 1 for alkali-metal atoms. If, instead, we choose pseudo-Hamiltonians \hat{h}_r [Eq. (7)] to approximate the electron-ion interaction, the f sum gives

$$N^{\text{PH}} = 1 + \int dr r^2 \rho(r) [a(r) + \frac{2}{3} b(r)] \quad (10)$$

(ρ , the electron density, is R_{1s}^2 for the atom) and again, when the pseudo-Hamiltonian reduces to an angular-momentum independent Hamiltonian [$a(r) = b(r) = 0$], we recover the standard sum rule. The results for the modified f sums N^{PP} and N^{PH} are shown for the alkali-metal atoms in the first two columns of Table III. Pseudopotentials and pseudo-Hamiltonians are here in good agreement. There is a clear trend in the f -sum rule, which is ≤ 1 for Li, and ≥ 1 for all the other alkali-metal atoms. If those results are compared with the actual number of valence electrons $N_v = 1$, as it seems most natural to do, one finds a lack of oscillator strength in the absorption spectra of Li, and a surplus for the other pseudoatoms. What is the meaning of such an “effective number of electrons,” and, if any, is pseudopotential theory the appropriate tool to estimate it? As already pointed out long ago by Fano and Cooper,¹⁴ in a many-electron system one cannot identify the sum partial sum of the oscillator strengths over a limited energy range (in our case the valence excitations only) with the corresponding number of “active” electrons (in our case the valence electrons): even when core and valence excitations are well separated in energy, the f sum over the allowed valence excitations is in general not equal to $N_v/2$, as a simple consequence of the Pauli principle. This effect, however, always yields a transfer of oscillator strength *from* the core *to* the valence, in such a way that, whenever applicable, it always increases the f sums with respect to the actual number of valence electrons. For what interests us here, the Fano-Cooper effect applies to all alkali-metal atoms except Li, for which no dipole transition connects the $1s$ core and the $2s$ valence states.¹⁴ The Fano-Cooper picture suggests that the f sums predicted by pseudopotentials and pseudo-Hamiltonians for Na, K, Rb, and Cs ($N^{\text{PP}}, N^{\text{PH}} \geq N_v = 1$), shown in the first two columns of Table III, are physically plausible, while the lack of a few percent of oscillator strength obtained for Li is not. The comparison of the partial contributions to the f sums due to the discrete spectrum with the corresponding restricted experimental

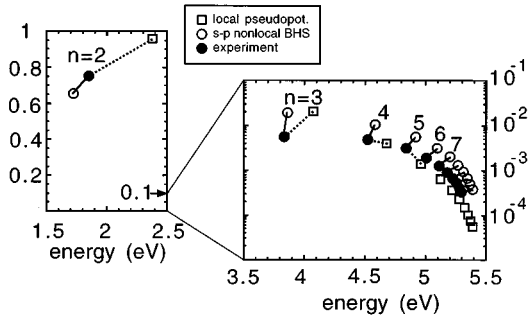


FIG. 2. Oscillator strengths for the 12 lowest dipole excitations of the lithium atom as a function of the excitation energy, as obtained from experiments (full circles, Ref. 28), from nonlocal pseudopotentials (empty circles, Ref. 18) and from a local potential recently adopted for lithium clusters (empty squares, Ref. 29). Notice that most of the total oscillator strength belongs to the first $2s$ - $2p$ transition (left panel), while the subsequent 11 transitions (shown in the right panel) are less strong by more than one order of magnitude. To help the eye, solid lines connect experimental points with the theoretical results of nonlocal pseudopotentials, and dotted lines with those of a local pseudopotential.

sums,²⁸ help us understand the origin of this slightly unphysical result for Li. If we only consider the discrete spectrum, as done in the last two columns of Table III, we find good agreement with the experimental values for all atoms including Li. The individual values and the trend show that first-principles pseudoions adequately reproduce the transfer of oscillator strength from core to valence states, a physical effect which occurs in the true, full-core ions.¹⁴ It may be interesting to see that for Li the use of first-principles, angular-momentum-dependent pseudoions is in fact necessary to reproduce the correct oscillator strengths as a function of energy: when, instead, a local pseudopotential is used to approximate Li, as done by, e.g., Blundell and Guet for Li clusters,²⁹ the sum rule is certainly obeyed for purely mathematical reasons, but the individual low-energy excitations (energy position and oscillator strength) are in much worse agreement with the optical data. This is shown in Fig. 2, where the Li oscillator strengths f_{0k} are plotted as a function of energy for nonlocal pseudopotentials (empty circles) experiments (full circles), and a simple local pseudopotential²⁹ (empty squares). Let us have a closer look at Fig. 2. If a local pseudopotential is used (empty square), both the energy position and the oscillator strength of the first s - p transition ($n=2$, left panel) are considerably misplaced with respect to the experimental value (full circle). In particular, the experimental first transition is located at about 1.8–1.9 eV, and its oscillator strength is 0.75, while the local pseudopotential predicts an energy around 2.4 eV and an oscillator strength as high as 0.96. The nonlocal pseudopotential (empty circle) falls much closer to the experimental value: it slightly undershoots it, with a transition energy of 1.7 eV and an oscillator strength of 0.65. The magnitude and energy position of the tiny oscillator strengths for the subsequent transitions $n=3 \dots 12$ (right panel; note the change in the scale) show a fair but uniform agreement between experiment (full circles) and nonlocal pseudopotential theory (empty circles), while for the local pseudopotential all the oscillator strengths with $n>4$ are off by almost an order of

magnitude. The most important error of the local pseudopotential theory concerns the lowest excitation ($2s$ - $2p$, left panel), but has important consequences also on the high-energy continuum tail of the spectrum, because of the sum rule: for the local model the total oscillator strength is practically exhausted by the discrete spectrum, which adds up to 0.99, so that practically nothing is left to the high-energy continuum (not shown in the figure); both the experiment and the nonlocal pseudopotential theory are instead characterized by a non-negligible high-energy continuum tail which contains approximately 25% of the total oscillator strength. In other words the local model puts too much oscillator strength in the low-lying excitations, and thus artificially sucks down to lower energies practically all of the oscillator strength of Li, while the nonlocal model approximately reproduces the experimental spectroscopic behavior at these energies. In conclusion, an angular-momentum-dependent pseudoion is absolutely needed to explain the lithium discrete spectrum; also for the other alkali-metal atoms both pseudo-Hamiltonians and pseudopotentials give a $\sim 5\%$ agreement between theory and experiments, which implies a good transferability for both of them in the low-energy portion of the spectrum (~ 5 eV above the atomic ground-state). As a consequence, even for Li, which unlike the heavier alkali-metal atoms has a lot (about 30%) of oscillator strength in the medium- and high-energy tail of the spectrum (the continuum part), the total sum rule (which according to the Fano-Cooper theory and the experiment should be 1) deviates only, as we see in the first two columns, by 3% and 7% for pseudo-Hamiltonians and pseudopotentials, respectively, which seems to be within the general accuracy of our pseudoions. However, for the medium- and high-energy portion of the excitation spectrum, (which for atoms is covered by the continuum) individual transition energies and oscillator strengths will sooner or later depart from the true atomic behavior, because of transferability problems intrinsic to the full pseudotransformation. The deviations will be larger for higher energies and/or for chemical environments increasingly different from the isolated atom (the so-called “reference state”,¹⁸). From this point of view the jellium density and a first-row pseudo-Hamiltonian²¹ represent the worst combination, which results, as seen, in an exaggerate effective mass and, by the same token, in an artificial loss of oscillator strength. Both transferability problems are much less severe if first-row nonlocal pseudopotentials are adopted.

IV. CONCLUSIONS

The nonlocal character of the effective electron-ion interaction “felt” by valence electrons has measurable consequences on optical properties of alkali-metal atoms, clusters, and bulk solids, which are greatest for Li. In the condensed state, more than half of the shift of its plasmon peak with respect to the predictions of the plain jellium model is due to the strong s - p nonlocality. Such a strong angular-momentum dependence is due to the fact that s valence electrons must remain orthogonal to a $1s$ core, while p valence electrons have no underlying core to be orthogonal to; this effect survives in the pseudo jellium model of Serra and co-workers.¹⁻³ The remaining part of the shift, however, is

essentially due to the discrete spatial arrangement of Li ions in the condensed state, and is wiped out by any jellium approximation. Here we confirm that one can adequately estimate both contributions using first-principles pseudopotentials,^{2,3} rather than empirically adjusting the nonlocal part, as done by Yabana and Bertsch, who first pointed out the twofold origin of the plasmon shift.⁸ First-principles nonlocal pseudopotentials also appear to be an adequate tool to evaluate energy positions and oscillator strengths for valence-only excitations: within a $\approx 5\%$ accuracy they reproduce the experimental individual excitations and f -sum rules, including the transfer of oscillator strength from core to valence states first pointed out by Fano and Cooper.¹⁴ From this point of view our study does not confirm the substantial ($\approx 25\%$) loss of oscillator strength from the f -sum rule, initially reported both experimentally⁷

and theoretically¹ for Li clusters. For the theory we have shown that the effect disappears using more accurate nonlocal pseudopotentials; the energy window and/or the technique adopted to infer oscillator strengths from cluster fragments might be the origin of the experimental “effect.”

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zero, but the expectation value over the ground state vanishes.

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