The Local-Plasma Approximation to the Oscillator-Strength Spectrum: How Good Is It and Why?

A procedure introduced by Lindhard and Scharff three decades ago enables one to evaluate the oscillator-strength spectrum solely from the ground-state charge distribution of any atom or molecule. In this procedure one regards an atom or molecule as consisting of small volumes that independently respond to an external uniform electric field in the same way as a free-electron gas. Some of the results of this procedure, called the local-plasma approximation, are remarkably realistic; an example is the mean excitation energy for stopping power in the Bethe theory. However, other results of the local-plasma approximation, most notably the oscillator-strength spectrum itself, are unrealistic in many respects, as we show below. This Comment discusses various consequences of the local-plasma approximation and points out its limitations. We also explain how difficult it is to derive the local-plasma approximation from first principles, i.e., starting with the standard definition of the oscillator strength in terms of the dipole matrix element and carrying out systematic mathematical operations.

INTRODUCTION

Lindhard and Scharff \textsuperscript{1} first used the idea of treating the atomic charge distribution as a local plasma to determine photoabsorption properties of atoms. In particular, they applied this idea to the calculation of the mean excitation energy $I$ in the Bethe expression for stopping power.\textsuperscript{2,3} Recall that an electron gas of uniform density $\rho$ oscillates with a single frequency, i.e., the plasma frequency:

$$\omega_p = \left(4\pi e^2 \rho / m_e \right)^{1/2}. \quad (1)$$
Assume also that each volume element in an atom contributes independently to the absorption strength. Then, an atomic charge distribution can be thought of as directly approximating the absorption spectra. That is, for every volume element the local density $\rho(r)$ at position $r$ determines the absorption frequency given by Eq.(1). The strength associated with each absorption frequency is equal to the amount of charge at the given density. Hence, the mean excitation energy $I$ is calculated for an atom as

$$Z \ln I = \int \rho(r) \ln(\hbar \omega_p) \, d^3r,$$

where $Z$ is the atomic number. If one uses the Thomas–Fermi density for $\rho(r)$, then one has a scaling relation $I/Z = \text{const.}$, in agreement with the result of Bloch\textsuperscript{4} for the hydrodynamic oscillation of the Thomas–Fermi atom. This scaling relation is roughly consistent with experimental observations for large $Z$, i.e., $I/Z \approx 10$ eV.

Lindhard and Scharff argued that the above description gave an estimate for the strength of absorption due to collective excitations in atoms. They further argued that single-particle excitations in heavy atoms were comparable to the collective excitations in their net contributions to $I$ but dominated the estimate of $I$ for light atoms. They therefore calculated $I$ from

$$Z \ln I = \int \rho(r) \ln(\gamma \hbar \omega_p) \, d^3r,$$

where $\gamma^2$ is a quantity between 1 and 2 included to account for these single-particle excitations. Using the Thomas–Fermi charge distribution and also Hartree distributions for a couple of atoms they obtained reasonable agreement with measured values setting $\gamma = \sqrt{2}$. Later Chu and Powers\textsuperscript{5} performed extensive calculations of $I$ for atoms using Hartree–Slater (HS) wavefunctions for evaluating the charge density and $\gamma = \sqrt{2}$. Use of such wavefunctions, as opposed to the use of Thomas–Fermi densities, led to a shell structure effect in $I$; that is to say, the resulting $I/Z$ value showed a periodic behavior as a function of $Z$ which tended to damp at higher $Z$, in agreement with experiment. Although the use of Hartree–Slater wavefunctions for calculating a collective effect has to be seriously questioned, the above prescription seems to allow one to calculate $I$ with some confidence and has recently been applied to molecules.\textsuperscript{6,7}
Inokuti and co-workers\textsuperscript{8-10} used the Hartree–Slater wavefunctions to calculate the photoabsorption (oscillator-strength) spectrum from the standard expression in terms of the dipole matrix element for atoms with $Z = 2$ to $Z = 38$. The oscillator strengths calculated in this manner can be reasonably thought of as describing the single-particle excitation spectra. In terms of the oscillator-strength spectra $df/dE$ the mean excitation energy $I$ is calculated from

$$Z \ln I = \int \ln E \left( \frac{df}{dE} \right) \, dE.$$  \hspace{1cm} (4)

Quite remarkably, Inokuti and co-workers found that their results were close to those of Chu and Powers in the $Z$ dependence and also in magnitude if $\gamma$ is set equal to one in the latter. This would seem to support the Lindhard–Scharff supposition that in some sense the oscillator-strength spectra determined in the \textit{local-plasma approximation} (LPA) describe single-particle excitations, at least for the purpose of calculating an averaged quantity such as $I$.

A direct averaging procedure like the LPA is much easier to apply than solving for the full photoabsorption spectra through matrix element evaluation when calculating an atomic property such as $I$, and thus is attractive if the procedure is justifiable from a basic point of view. Therefore, one can reasonably ask what other properties of the spectra can be estimated with a similar accuracy, and how good the LPA is as an approximation to the photoabsorption spectra itself. More importantly, one would like to know \textit{why} the LPA gives such reasonable values for $I$. It is certainly not obvious that the calculation of Chu and Powers and that of Inokuti and co-workers should lead to similar results. In what follows we will discuss what the limitations of the LPA are and when this method may be used with reasonable confidence. Furthermore, one would like to derive the LPA approximation starting with the standard definition of the oscillator-strength spectra. Here we discuss the difficulties in carrying out such a program and pose it as an important question to be answered.

**THE LPA**

Brandt and Lindqvist\textsuperscript{11} and Brandt \textit{et al.}\textsuperscript{12} have employed the LPA to estimate the photoabsorption spectrum for large $Z$ atoms. Ac-
According to the LPA the atomic oscillator-strength spectrum is given as

\[ \frac{df}{dE}^{\text{LPA}} = \int \rho(r) \delta[E - \gamma \omega_p(r)] \, d^3r. \]  

Equation (5) is indeed a mathematical expression of the prescription of Lindhard and Scharff. That is, Eq.(5) says that the frequency given by Eq.(1) is associated with each region of charge density, and substituting Eq.(5) into Eq.(4) one obtains Eq.(3). Brandt and Lindqvist\textsuperscript{11} and Brandt \textit{et al.}\textsuperscript{12} have justified the use of Eq.(5) in Eq.(4) by pointing out that the photoabsorption spectra of large Z atoms are dominated by collective excitations and that the LPA should describe such effects. Fano and Cooper\textsuperscript{13} discuss the relation between the collective excitations and single-particle excitations. They show the two concepts are different starting points in successive approximations to the properties of atoms. They further show by considering a few examples that in some cases one or the other may provide a better zeroth-order estimate of the photoabsorption spectrum. Both these starting points can in principle be used to determine an accurate photoabsorption spectrum if a suitable perturbation scheme is carried out to include residual effects. Fano and Cooper discuss corrections to the single-particle spectrum for the collective effects (i.e., correlation or configuration-mixing effects) and indicate when such effects are large. However, an alternative procedure beginning with the LPA has not been systematically developed; indeed, not even a rigorous derivation of the LPA is known. Brandt and Lindqvist and Brandt \textit{et al.} outline the physical nature of improved collective approximations. But to the best of our knowledge no scheme based on the exact expression for the oscillator-strength spectrum has been presented for systematically determining corrections to the free-electron picture.

A starting point for understanding the LPA is to write the oscillator-strength spectrum as\textsuperscript{13}

\[ \frac{df}{dE} = (2\pi \hbar)^{-1} \int_{-\infty}^{\infty} dt \exp(-iEt/\hbar) \left\langle \phi(t) \right\rangle, \]  

where the brackets indicate the ground-state expectation value of the operator \( \phi(t) \). The LPA amounts to setting

\[ \phi^{\text{LPA}}(t) = \sum_j \exp[i\gamma \omega_p(r_j)t], \]
where \( r_j \) is the position of the \( j \)th atomic electron. In contrast, the exact expression is

\[
\phi(t) = [x^t(t) p - px(t)]/i\hbar,
\]

where \( x(t) = e^{iHt/\hbar}x e^{-iHt/\hbar}, H \) is the atomic Hamiltonian, \( x \) is the sum of electron coordinates and \( p \) is the sum of electron momenta. (\( x \) and \( p \) here represent a Cartesian component taken along the light polarization; the direction is immaterial so long as we presume random orientation of atoms or molecules.)

One may expand these expressions [Eqs. (6) and (7)] in powers of \( t \) and compare each of the terms that arise upon substitution into Eq. (6). This is equivalent to considering various moments of the distribution \( df/dE \), referred to as the sum rules:

\[
S_n = \int E^n(df/dE) \, dE.
\]

The derivatives of these quantities with respect to \( n \) are also useful in applications. They may be defined as

\[
L_n = dS_n/dn = \int E^n\ln E(df/dE) \, dE;
\]

for instance, \( L_0 \) defines \( I = \exp(L_0/S_0) \). Within the LPA the sums have the form

\[
S_n^{\text{LPA}} = \langle \Sigma_j [\gamma \hbar \omega_p(r_j)]^n \rangle,
\]

which, using Eq.(1), can be seen to be finite for any \( n > -2 \). By contrast, the exact sums are finite only for \( n < 2.5 \). This difference already indicates that the LPA expression for the oscillator strength cannot be accurate at large or small energies. The LPA expression leads to a maximum absorption energy corresponding to the maximum electronic density (which usually occurs at the nucleus according to numerical calculations) and gives rise to no finite low energy threshold. This unrealistic result is a consequence of the fact that the charge density takes on all values between zero and the maximum. The failure at small energies (which govern the values of \( S_n \) for \( n < 0 \)) can be understood by noting that the LPA is meaningful only if both the volume element of interest is large enough to contain a number of electrons but is at the same time small enough so that the density can be assumed to be uniform. This of
course breaks down in the exponentially decreasing tail of the atomic wavefunction. The failure at large energies (which govern the values of $S_n$ for $n > 0$) results from the following related circumstance: The finite electron density near the nucleus limits the absorption frequency in the LPA, whereas an electron bound in a Coulomb field near the nucleus can absorb an arbitrarily large amount of energy, albeit with a low probability. At best, therefore, the LPA can be used to estimate quantities that are determined by the sums or the derivatives of the sums $2.5 > n > -2$. The sum with $n = 0$ represents a normalization condition and is the same for the LPA and the exact expression.

Examination of $S_2$ clarifies the differences in the two spectra. Applying operator methods to the expression $x(t)$ one obtains for $\gamma = 1$,

$$
S_2^{\text{LPA}} = (\hbar^2/2m_e) \langle 4\pi e^2 \sum \rho(r) \rangle,
$$

(12)

to be compared with the exact expression

$$
S_2 = (\hbar^2/2m_e) \langle (-1/3) \sum \nabla_j^2 V \rangle.
$$

(13)

Here we assume a spherically symmetric charge distribution, $\nabla_j^2$ is the Laplacian for the electronic coordinates and $V$ is the potential of the electrostatic forces acting on the atomic electrons. Because the Laplacian of $V$ is the charge density according to the Poisson equation, the results in Eqs.(12) and (13) are tantalizingly similar. However, the factor of $1/3$ illustrates a fundamental problem when one tries to relate the LPA to the exact photoabsorption spectrum: The expression in Eq.(13) is an average of particle properties whereas the expression in Eq.(12) is not. Therefore, a simple replacement of $H$ in Eq.(8) by an approximate Hamiltonian cannot yield the LPA expression in Eq.(7). For this reason, any derivation of the LPA must begin within an expression for which the charge-density fluctuations can be considered. Nevertheless, the two expressions may lead to similar results because the integrands in both Eqs.(12) and (13) are peaked at the nucleus.

To incorporate the charge-density fluctuations we write $\phi(t)$ in Eq.(6) in terms of the autocorrelation function:

$$
\phi(t) = \lim_{k \to 0} \langle 2iEm_e/\hbar^2 k^2 \rangle \left[ \rho_k(0) \rho_k(t) - |\langle \rho_k(t) \rangle|^2 \right],
$$

(14)
where \( \rho_k(t) = \sum_{j=1}^{Z} \exp i(k \cdot r_j) \) indicates the electron density fluctuations associated with momentum \( \hbar k \). Bohm and Pines\textsuperscript{14} earlier showed that \( \rho_k(t) \) oscillates with \( \omega_p \) for a free-electron gas with a uniform positive charge background. Dividing the atom into regions of nearly constant density one can again expect that an expression like the desired result in Eq.(5) may be obtained. From these arguments restrictions on \( k \) can be made. Clearly we must require that \( k \gtrsim |(d \psi/dr)/\psi| \sim 1/\tilde{a} \) for the density to be nearly constant, where \( \psi \) is the atomic wavefunction and \( \tilde{a} \) is the atomic radius, but we must have \( k << 1/\tilde{a} \) in order to satisfy approximately the dipole limit \( k \to 0 \). This contradiction suggests the LPA procedure as applied to atoms may not be physically sound. In other words, most of the atomic electrons are so strongly bound that their dynamics are far from that of the free-electron gas.

Finally, an analytic property of the correct oscillator-strength spectrum may be mentioned. As Dillon and Inokuti\textsuperscript{15} showed, the correct spectrum, considered as an analytically continued function of the complex variable \( E \), has singularities at \( E = -J_s \), where \( J_s \) is the threshold energy for each subshell \( s \). (In addition, there may be other singularities associated with bound states and resonances.) The singularities at \( E = -J_s \) are obviously outside the domain \( E > 0 \) of direct physical measurements, but are important in determining the overall behavior of \( df/dE \) at low \( E \). The LPA expression, Eq.(5), contains no mathematical element giving rise to these singularities.

LPA SPECTRA

Leaving aside the issue of a mathematical derivation of the LPA method, one may instead compare the LPA photoabsorption spectra with other calculations. In Figure 1 we compare the LPA spectrum for a Thomas–Fermi atom with the oscillator-strength spectrum as determined by Ball et al.\textsuperscript{16} from the Bloch hydrodynamic model.\textsuperscript{4} To obtain LPA spectrum we rewrite Eq.(5) in the form

\[
(df/dE)_{\text{LPA}} = \frac{8\pi}{\alpha} \left[ r^2 \left| \frac{dr}{dp} \right| p^{3/2} \right],
\]  
(15)
where $\rho$ is to be equated with $(E/\alpha)^2$, and $\alpha^2 = 4\pi e^4 a_0$. (Note that $df/dE$ is not continuous unless $\rho$ is a monotonically decreasing function of $r$.) A striking similarity is seen between the two spectra in Figure 1. Furthermore, they scale with $Z$ in the same way. This comparison confirms the notion that the LPA can describe to some extent collective (hydrodynamic) oscillations in a statistical model of the atom. However, the values of $I$ determined from these spectra differ appreciably; $I/Z = 4.95$ eV for the spectrum of Ball et al.\textsuperscript{16} and $I/Z = 6.2$ eV for the LPA spectrum. More strikingly, both of these results differ considerably from the empirical value of $I/Z \approx 10$ eV at large $Z$; indeed, the discrepancy of the LPA value of $I/Z$ from the empirical value was probably the origin of the ad hoc introduction of $\gamma$ by Lindhard and Scharff.\textsuperscript{1} This disagreement of the $I/Z$ value of Ball et al.\textsuperscript{16} with the empirical value of $I/Z$ may be of some concern because it has been shown\textsuperscript{17,18} that the Thomas–Fermi charge distribution for atoms is \textit{exact in the limit of large} $Z$. 

\textsuperscript{17,18}
Most likely, the dynamics of real atoms (with $Z \leq 100$) is still so far away from the exact high $Z$ limit that the above comparison of the $I/Z$ values is not fully justified.

As Brandt and Lindqvist\cite{11} and Brandt et al.\cite{12} showed, the use of an electron density showing shell structure in the LPA usually leads to some shell-structure effect in the oscillator-strength spectra. In Figures 2 and 3 we compare the spectra for Ar and Na (calculated by Inokuti and co-workers\cite{8}) with the LPA approximation evaluated using Hartree–Slater wavefunctions. Indeed, structures are seen in the LPA spectra, but these structures are often unrealistic; for instance, the maxima in the LPA do not generally correspond to spectroscopically well known shell threshold energies. In this sense the LPA spectrum differs much from the spectrum obtained by the matrix element evaluation and also from experi-

![Graph](image.png)

**FIGURE 2** The oscillator-strength spectra for argon. Note that the plot is doubly logarithmic. The long-chained curve (—— — — — —) represents the Thomas–Fermi spectrum as obtained by Ball et al.\cite{16} The broken curve (— — — —) represents the local-plasma approximation with the use of the Hartree–Slater density. The solid curve represents the result of matrix element calculations based on the Hartree–Slater potential\cite{5}; the discrete spectra are also included after smoothing. The solid curve shows every shell threshold closely agreeing with experiment. The undulations of the short-chained curve are a consequence of the shell structure seen in the Hartree–Slater density but are unrealistic.
FIGURE 3 The oscillator-strength for sodium. See caption to Figure 2.

ment. This conclusion should apply generally: The two atoms for which the oscillator-strength spectra are shown are representative in that one is a closed-shell system and the other has a single electron in the outer shell.

Figures 2 and 3 show that the oscillator-strength spectrum for the Thomas–Fermi hydrodynamic model gives a better overall description of the spectra than the LPA over most of the energy range, failing only at high and low energies. The LPA moments (Table I), however, are more reasonable mainly because of the high frequency cutoff in the LPA. For Ar and Na the LPA values for $S_{-1}$, as well as for $L_{-1}$, agree well with the results of the matrix element calculation. However, the LPA moments become increasingly unrealistic as $n$ differs further from $n = 0$; this is particularly notable in the $L_{-1}$ values (which represent the slope of the $S_n$ versus $n$ curve) and also in the values of $S_1$ and $L_1$ (Table I).

Table I also shows the oscillator-strength moments for the hydrogenic atom, i.e., an atom with a single electron in the Coulomb field of charge $z e$. Here the discrepancies between the truly exact result and the LPA result are most evident. In particular, the difference in the $z$ dependence of all the quantities (except for $S_0$) is most notable.
### TABLE I.
Moments of the oscillator-strength spectra

<table>
<thead>
<tr>
<th></th>
<th>Ar(^b)</th>
<th>Na(^b)</th>
<th>Hydrogenic atom with nuclear charge(Ze)</th>
<th>Thomas–Fermi model for atomic number(Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exact(^c)</td>
<td>LPA</td>
<td>Exact</td>
<td>LPA(^d)</td>
</tr>
<tr>
<td>(S_{-1})</td>
<td>10.2</td>
<td>10.7</td>
<td>15.2</td>
<td>16.5</td>
</tr>
<tr>
<td>(S_0)</td>
<td>18.0</td>
<td>18.0</td>
<td>11.0</td>
<td>11.0</td>
</tr>
<tr>
<td>(S_1)</td>
<td>(5.8 \times 10^2)</td>
<td>(2.7 \times 10^2)</td>
<td>(7.6 \times 10^2)</td>
<td>(1.0 \times 10^2)</td>
</tr>
<tr>
<td>(L_{-1})</td>
<td>-2.12</td>
<td>-8.61</td>
<td>-29.8</td>
<td>-41.6</td>
</tr>
<tr>
<td>(L_0)</td>
<td>33.5</td>
<td>30.3</td>
<td>16.7</td>
<td>14.8</td>
</tr>
<tr>
<td>(L_1)</td>
<td>(2.9 \times 10^3)</td>
<td>(0.96 \times 10^3)</td>
<td>(7.8 \times 10^2)</td>
<td>(3.0 \times 10^2)</td>
</tr>
</tbody>
</table>

\(^a\) All the quantities are defined in terms of the excitation energy measured in atomic units (27.2 eV).
\(^b\) The argon atom and the sodium atom are both treated within the Hartree–Slater approximation.
\(^c\) The data are due to Inokuti and co-workers (Refs. 8 and 9).
\(^d\) The oscillator-strength spectrum within the LPA is given by \(df/dE = 4(U/E^2)\ln(E/U)^2\), where \(U = 2z^{3/2}\) is the maximum energy of absorption. Hence, one obtains \(S_n = 8(2 + n)^{-3}U^n\) and \(L_n = S_n\ln[Ue^{-3(2+n)}]\) for any \(n > -2\).
\(^e\) The data are due to Ball et al.\(^{16}\).
CONCLUDING REMARKS

Numerical comparison has shown that the LPA is a reasonable approximation to the Thomas–Fermi oscillator-strength spectrum evaluated in the Bloch hydrodynamic model. This comparison confirms the suggestion that the LPA describes collective oscillations to some extent. However, both the LPA result for $I$ and the calculation of $I$ by Ball et al.$^{16}$ are appreciably different from the empirical value at high $Z$.

The question remains whether a mathematical derivation of the LPA can be found, or at least whether one can demonstrate from first principles the reasonable values of the lower order moments of the oscillator-strength distribution. Those reasonable values of the mean excitation energy $I$ are particularly surprising because the LPA does not describe the shell structure of the oscillator-strength spectra correctly. The agreement is probably attributable to the fact that the value of the mean excitation energy $I$ is chiefly determined by the spectrum at intermediate energies.

There is a basic inconsistency in the idea of the LPA viewed as a method of evaluating the photoabsorption intensity. To start with, the plasma in a pure free-electron gas is a longitudinal mode of excitation. It is therefore inaccessible by the absorption of photons, as one readily sees in the plasma due to conduction electrons in a metal. In a medium with a nonuniform electron density the distinction between a longitudinal mode and a transverse mode is no longer sharp, and as a result some plasma excitation is possible by photoabsorption. A mathematical expression of this circumstance would be a key element in a derivation of the LPA from first principles.

Finally, it may be added that an idea basic to the LPA is sometimes applied to specific goals other than the direct evaluation of the oscillator-strength or its moments from the charge distribution alone. For example, certain corrections to the static Hartree–Slater potential have been treated$^{19}$ from a point of view closely related to the LPA with considerable success.

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