

## Geometrical basis for molecular stopping anisotropy

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We consider the effect of shape on the anisotropy of stopping of swift ions by molecular targets. By use of an anisotropic harmonic-oscillator model and frequencies based on jellium ellipsoids, we show that a meaningful estimate of molecular stopping anisotropy can be obtained from molecular shape alone.

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### I. INTRODUCTION

The anisotropy in energy deposition by swift ions in molecular targets is a subject of increasing interest, given the advent of ever more accurate methods for orienting molecular target systems and for measuring energy loss [1–3]. In a pair of recent papers [4,5], the topic was considered for several molecules in some detail. Bethe theory was invoked and the stopping anisotropy calculated from the directional dependence of independently calculated mean excitation energies. A clear correlation of stopping anisotropy with molecular shape emerged. The effect was found to be of the order of 5% of the total stopping cross section. The underlying physics of that correlation is investigated here.

The interpretation that emerges is based on the following line of argument. At least roughly, the electrons in a molecule average out the details of ionic positions. Accordingly, one may model the ionic background as jellium with an anisotropic boundary to include effects of the overall shape. For such a situation the electrons move in an anisotropic confining potential that is harmonic and the characteristic harmonic frequencies coincide with the surface plasmon frequencies of the corresponding jellium ellipsoid. The harmonic potential theorem [6–8] then states that independent of the electron-electron interaction, those frequencies are the excitation frequencies of the system. Hence both the average stopping energy and its anisotropy will be related to those frequencies.

Oscillator models have been used frequently in nuclear, cluster, and surface physics to predict general trends [9,10]. One example is the Clemenger model [11] for metal clusters that is based on the Nilsson model [12] for nuclei. In essence, the valence electrons are assumed to move in an effective one-electron potential approximated by an anisotropic (an)harmonic oscillator. For small clusters the anharmonic contributions can be neglected. Trends for global cluster properties seem to be well predicted, even for small numbers of particles in the cluster [9,10]. At the same time measurements of photoabsorption cross sections in small alkali-metal clusters have shown the existence of resonant features that can be seen as surface collective (plasmon) excitations [13,14]. Observed double and triple peaks can be associated with surface plasmons in clusters of *ellipsoidal*

shape, i.e., nonspherical clusters [14]. See Fig. 1. Hence our approach is to use a harmonic-oscillator model for molecules with the characteristic excitation frequencies of jellium ellipsoids as input.

The rationale rests, as mentioned above, on the fact that details of ionic core structure affect the excitation spectrum of the valence electrons only slightly (the justification for using effective core potentials for example); hence, in the simplest approximation one may neglect the detailed ionic core structure [9,15] and treat the cores as simply providing the neutralizing background. We thus compare stopping anisotropies for several small molecules based on input from jellium ellipsoids with the results calculated by substantially more detailed and rigorous methods of molecular quantum mechanics [4,5]. The comparison should be useful in the sense of giving both preliminary and interpretive estimates of molecular stopping anisotropy.

Section II first introduces and defines stopping asymmetry and then outlines the relationship between the shape and collective excitation frequencies in a jellium ellipsoid and the same relationship based on another simple and useful model: the single-particle Clemenger model [11]. Section III shows

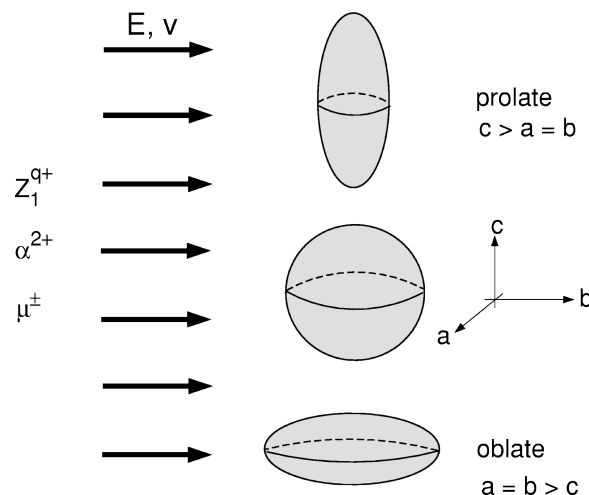


FIG. 1. Jellium ellipsoids of rotation oriented with respect to the incoming projectile velocity. Stopping anisotropies in small molecules can be understood on a geometrical basis alone; i.e., the ratio between  $a (=b)$  and  $c$ .

that the collective excitation frequencies of jellium ellipsoids happen to enter the single-particle energies in a harmonic-oscillator model of the molecule since they determine the curvature of the harmonic potential. Thus a model that merges the prior two is given in Sec. III and then is used to give the theoretical foundation for the stopping asymmetry from shape. As an illustrative test, a group of molecules is mapped into ellipsoids by using tabulated bond lengths and van der Waals radii, whence we find good agreement (within 10%) between the simple estimate and the detailed, fully quantum-mechanical molecular treatment.

## II. THEORETICAL BACKGROUND

In this section we define the stopping asymmetry and delineate two simple models to calculate it. The first introduces the relationship between shape and excitation frequencies for ellipsoidal jellium particles. The second is the single-particle Clemenger model for clusters, which provides another relationship between excitation energies and shape.

### A. Stopping asymmetry

The linear energy deposition for a spheroidal target oriented with its major symmetry axis parallel to the laboratory  $z$  axis can be written [4]

$$-\left(\frac{dE}{di}\right) = nS^i(v), \quad (1)$$

with  $i=x,y,z$  and  $n$  the number density of scatterers. For a beam oriented along the  $z$  axis the stopping cross section becomes

$$S^z(v) = \frac{Z_1^2 Z_2 e^4}{4\pi m v^2 \epsilon_0^2} \ln \frac{2mv^2}{I_0^x}, \quad (2)$$

while for a beam perpendicular to the  $z$  axis [4]

$$S^x(v) = \frac{Z_1^2 Z_2 e^4}{4\pi m v^2 \epsilon_0^2} \ln \frac{2mv^2}{\sqrt{I_0^x I_0^z}}. \quad (3)$$

Here  $Z_1$  is the projectile charge,  $Z_2$  the number of scattering electrons in the target molecule (or cluster), and  $v$  the projectile velocity in the laboratory frame. The directional components of the mean excitation energy  $I_0^i$  are defined in terms of the corresponding components of the dipole oscillator strength distribution  $f^i(E)$  of the target:

$$\ln I_0^i = \frac{\int f^i(E) \ln E dE}{\int f^i(E) dE}. \quad (4)$$

For a molecule with full rotation symmetry about the  $z$  axis (e.g.,  $C_{\infty v}$ ), the directional difference in stopping is

$$\Delta S(v) \equiv S^x(v) - S^z(v) = \frac{Z_1^2 Z_2 e^4}{8\pi m v^2 \epsilon_0^2} \ln \frac{I_0^x}{I_0^z} \quad (5)$$

and an obvious anisotropy parameter [1] is

$$A = \ln \frac{I_0^x}{I_0^z}. \quad (6)$$

The question arises as to the extent to which this anisotropy can be associated with the molecular shape alone and thus whether the shape itself can be used as a predictor of molecular stopping anisotropy.

### B. Jellium ellipsoids

In this section we connect stopping and collective excitation energies via electron gas considerations. Such connections have a venerable history in stopping theory, dating to the homogeneous gas calculation of Kramers [16] and the related local plasma approximation of Lindhard and Scharff [17].

A finite, nonspherical jellium object has collective electronic dipolar excitation frequencies associated with the direction  $i$ , which can be written as

$$\omega_p^i = \sqrt{n_i} \omega_p, \quad (7)$$

where  $\omega_p$  is the plasma frequency characteristic of the density of the smeared out ionic (jellium) background and  $n_i$  is a geometry-dependent depolarization factor [18,19]. We do not consider the bulk plasmon excitation since it is not shape dependent and hence drop it in Eq. (5).

Consider a jellium ellipsoid of revolution with rotational axis  $c$  and semiaxes  $a=b$  satisfying

$$\frac{x^2}{a^2} + \frac{y^2}{b^2} + \frac{z^2}{c^2} = 1 \quad (8)$$

and with eccentricity  $\varepsilon$

$$\varepsilon = \frac{1}{c} \sqrt{|a^2 - c^2|} \quad (9)$$

as in Fig. 1. We assume the jellium ellipsoids to have sharp boundaries and to consist of a uniform electron gas. In keeping with the aforementioned line of argument [16,17], it is reasonable to assume that the mean excitation energy in direction  $i$ ,  $I_0^i$ , is proportional to  $\omega_p^i$  since it is the only excitation frequency in this model (*vide infra*). The stopping anisotropy for such an ellipsoid then should be proportional to the ratio of the depolarization factors

$$\frac{I_0^x}{I_0^z} = \sqrt{\frac{n_x}{n_z}}. \quad (10)$$

The depolarization factors ( $0 \leq n_i \leq 1$ ) for a jellium ellipsoid can be written [18].

$$n_i = \frac{abc}{2} \int_0^\infty \frac{d\lambda}{(j^2 + \lambda) \sqrt{(a^2 + \lambda)(b^2 + \lambda)(c^2 + \lambda)}}, \quad (11)$$

where  $j=a,b,c$  in order when  $i=x,y,z$ . Consideration of oblate and prolate ellipsoids leads, after some algebra, to depolarization factors (in terms of the eccentricity  $\varepsilon$  [18,19]) of

$$n_z = \frac{1 + \varepsilon^2}{\varepsilon^3} (\varepsilon - \tan^{-1} \varepsilon), \quad (12)$$

$$n_z = \frac{1 - \varepsilon^2}{\varepsilon^3} \left[ \ln \sqrt{\frac{1 + \varepsilon}{1 - \varepsilon}} - \varepsilon \right] \quad (13)$$

for oblate and prolate ellipsoids, respectively.

Now  $n_x + n_y + n_z = 1$  and in the present case  $a = b$ , hence  $n_x = n_y = (1/2)(1 - n_z)$ . The ratio of the mean excitation energies perpendicular and parallel to the axis of rotation for such a jellium ellipsoid is then

$$\frac{I_0^x}{I_0^z} = \sqrt{\frac{1 - n_z}{2n_z}}. \quad (14)$$

Notice that the ratio is function of  $c/a$  alone [cf. Eqs. (9), (12), and (13)] and is unity for  $a = c$  (sphere). Thus the stopping anisotropy is a function of geometry only.

It should be noted that as a consequence of choosing  $\omega_p$  to be constant, the results discussed above have no overall scale except  $\omega_p$ . Thus the formulas and frequencies depend only on *form* and, in the absence of retardation effects, not on absolute dimension. Thus these formulas also should apply to large particles (e.g., nanoparticles). A practical retardation limit is reached, however, with particles of characteristic dimension of the order of 10–20 nm.

### C. Clemenger model

Another useful way of estimating stopping anisotropy is to use the Clemenger model [11]. In its simplest form (neglecting anharmonic terms), it is based on an effective single-particle Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2} m \omega_0^2 [\Omega_{\perp}^2 (x^2 + y^2) + \Omega_{\parallel}^2 z^2], \quad (15)$$

where the spheroidal scaling factors for the axes perpendicular and parallel to molecular symmetry axis,  $\Omega_{\perp}$  and  $\Omega_{\parallel}$ , may be expressed in terms of a distortion parameter  $\delta$  which to first order is the difference between the major and minor axes of an ellipsoid divided by the mean radius:  $\delta \approx 2(c - a)/(c + a)$ . The volume is constrained in the Clemenger model such that  $\Omega_{\perp}^2 \Omega_{\parallel} = 1$ , where  $\Omega_{\perp} = [(2 + \delta)/(2 - \delta)]^{1/3}$ . Clearly this Hamiltonian has characteristic energies  $\hbar \omega_0 \Omega_{\perp}$  and  $\hbar \omega_0 \Omega_{\parallel}$  for excitations perpendicular and parallel to the molecular symmetry axis. Therefore, the mean excitation energies in the Clemenger model should have the unique ratio [11]

$$\frac{I_0^x}{I_0^z} = \frac{\Omega_{\perp}}{\Omega_{\parallel}} = \Omega_{\perp}^3 \equiv \frac{2 + \delta}{2 - \delta} \approx \frac{c}{a}, \quad (16)$$

where the last approximation holds near sphericity. The more refined relationship  $\delta = (3/2)(c^2 - a^2)/(c^2 + 2a^2)$  [19] does not alter the qualitative directional behavior of the mean excitation energy ratio. There is clearly a connection between shape and mean excitation energies also in this model. Though not shown here for compactness, in fact, the basic Clemenger model gives somewhat steeper behavior than the

jellium model. In the next section we will utilize a Clemenger-like model but with another estimate of the single-particle excitation energies, based on the jellium approach.

## III. RESULTS AND DISCUSSION

We first show that the collective excitation frequencies of a jellium ellipsoid considered in Sec. II B can be used as the single-particle excitation energies in a harmonic-oscillator model such as the one in Sec. II C. We use this to provide an input in a stopping theory based on harmonic oscillators, hence to motivate a general relationship between stopping asymmetry and shape. We then map actual molecules into ellipsoids via a systematic recipe and compare the results for those molecules with the predictions for the equivalent ellipsoids in the improved model.

### A. Harmonic-oscillator model

The key elements of the previous sections are Eqs. (14) and (16) relating the asymmetry to the shape. One way to improve on the previous sections is to relate the energy scales in the Clemenger cluster model to a more detailed model of the molecules. The distortion  $\delta$  in the original Clemenger model was inferred from the sum of single-particle energies being a minimum.

For electrons confined to a jellium ellipsoid, the potential inside the sharp boundary has a curvature that coincides with the collective excitation frequencies. That is, internal to the sharp boundary of an ellipsoid, the confining potential  $V$  from the ellipsoidal jellium background is quadratic

$$V = \frac{m \omega_p^2}{2e} (n_x x^2 + n_y y^2 + n_z z^2 + C), \quad (17)$$

where  $C$  is a constant (cf. Eq. 20, in Ref. [19]) and the depolarization factors govern the geometric confinement. Assuming that the electrons do not sample the potential outside the jellium ellipsoid to any significant extent, the harmonic potential may be extended to that region with impunity. The whole object then may be treated as an anisotropic oscillator, similar to what has been done earlier in nuclear and cluster physics [9,10].

It is known that for such an anisotropic harmonic oscillator the excitation energies  $\omega_v^i$  are equidistant, but differ with direction

$$\omega_v^i = \nu \omega_0^i, \quad (18)$$

where  $\nu = 1, 2, 3, \dots$  and  $i = x, y, z$ . As always with harmonic systems,  $\omega_0^i$  is related to the curvature of the confining potential for the ellipsoid in direction  $i$ , in our case directly related to  $\sqrt{n_i} \omega_p$  according to Eq. (17).

Harmonic oscillator models have also been used to describe energy deposition [20–22]. In particular, there is a scheme based on the (quantum) harmonic oscillator for calculation of atomic stopping properties [23–25]. We can use those results (Eq. 27, Ref. [23]) to show that (to lowest order in  $\hbar \omega_0^i / 2mv^2$ , where  $\frac{1}{2}mv^2$  is the projectile kinetic energy) the mean excitation energy  $I_0^i$  is

TABLE I. Mean excitation energy ratios and geometrical parameters for some small molecules. The values for  $I_0^x$  and  $I_0^z$  are from [5]. The geometrical parameters (in angstroms) are from bond distances [27,28] and van der Waals radii [29].

Molecule	$(I_0^x/I_0^z)$	$a$	$c$	$a/c$
C <sub>2</sub> H <sub>2</sub>	1.308	1.65	2.962	0.557
HCN	1.259	1.60	2.710	0.590
CO	1.183	1.58	2.144	0.737
N <sub>2</sub>	1.209	1.55	2.099	0.738
CH <sub>4</sub>	1.000	1.744	1.744	1.000
NH <sub>3</sub>	0.943	2.238	2.088	1.072
BH <sub>3</sub>	0.859	2.833	1.80	1.574
C <sub>6</sub> H <sub>6</sub>	0.831	3.781	1.475	2.563

$$I_0^i = \hbar \omega_0^i \equiv \sqrt{n_i} \hbar \omega_p, \quad (19)$$

according to the arguments given above.

Observe that Sigmund and Haagerup [23] use individual atomic oscillators, while the frequencies entering here are characteristic of the confining potential of the ellipsoid as a whole. In alternative language, we utilize the single-particle energies of the harmonic oscillator that coincide with the plasma frequencies for the confining jellium ellipsoid. Only the first few excitations are important, as they are spaced rather far apart. This observation is consistent with our choice of continuing the harmonic potential beyond the jellium edge of the ellipsoid.

We note that this scheme, although approximate, incorporates a formally exact feature. The result is independent of electron mutual interactions. This is not to say that these interactions are zero, but rather that their introduction will not change the relationship among the excitation energies [Eq. (18)] [6,7,26]. The model should work best, however, for cases in which the low-lying excitations dominate; for them the extension of the quadratic potential is not such a severe approximation. To summarize this section our prediction is that the stopping asymmetry  $I_0^x/I_0^z = \sqrt{n_x/n_z}$ , the same as in the plasma model of Sec. II B, but for a different reason based as it is on single-particle energies. The connecting reason is of course that the jellium background is providing the restoring force both for the collective excitations and the confinement of the electrons to its interior.

### B. Molecular mean excitation energies

To check the proposition that stopping anisotropy is primarily dependent on molecular geometry against independent molecular data, we need molecular directionally dependent mean excitation energies and geometric parameters. Such quantities are available from previous polarization propagator calculations [5] that utilized rather large basis sets and included electron correlation at the level of the random-phase approximation. Calculations of this degree of refinement have proved reasonably reliable in past applications.

The determination of appropriate molecular geometrical parameters is a more subtle matter. For simplicity, we consider molecules with high axial symmetry and assume that each can be represented adequately for the present purpose by an ellipsoid with a major axis of length  $c$  pointing along

TABLE II. The mean excitation energy ratios and geometrical parameters for H<sub>2</sub>.  $I_0^x$  and  $I_0^z$  are from [30]. The aspect ratio  $a/c$  is a fixed volume, while  $(a/c)^*$  values are without that constraint; see the text.

$R_{HH}$ (a.u.)	$(I_0^x/I_0^z)$	$a/c$	$(a/c)^*$
0.70	1.111	0.799	0.788
1.10	1.211	0.709	0.703
1.4011 ( $R_{eq}$ )	1.287	0.650	0.650
1.70	1.363	0.598	0.605
2.10	1.452	0.537	0.553

the  $C_n$  rotational axis. We choose  $c$  and  $a=b$  by combining tabulated bond lengths [27,28] and van der Waals radii [29]. At the least, this mapping of molecules to ellipsoids is systematic and well defined. The mapping results in the data in Table I for several representative molecules.

A similar set of data can be generated for H<sub>2</sub> as a function of bond length  $R_{HH}$ . Using previously determined directional mean excitation energies as a function of  $R_{HH}$  [30] and constraining the volume of the prolate ellipsoid (determined by the method just described) to be constant, we obtain the data in Table II. For comparison we show the values  $a/c$  if the volume is not kept fixed [denoted by  $(a/c)^*$ ].

### C. Comparisons

The molecular directional mean excitation energies vs  $a/c$  from Table I are shown in Fig. 2 along with the curves obtained in a Clemenger harmonic-oscillator model (dashed curve) [Eq. (16) with  $\delta = (3/2)(c^2 - a^2)/(c^2 + 2a^2)$ ] and for a harmonic-oscillator model with jellium input from Sec. III A (full curve). We see that the latter model does a better job than the former. Similarly, the data in Table II for mean excitation energies vs  $a/c$  as a function of bond length in H<sub>2</sub> are plotted in Fig. 3, along with the curve for the correspond-

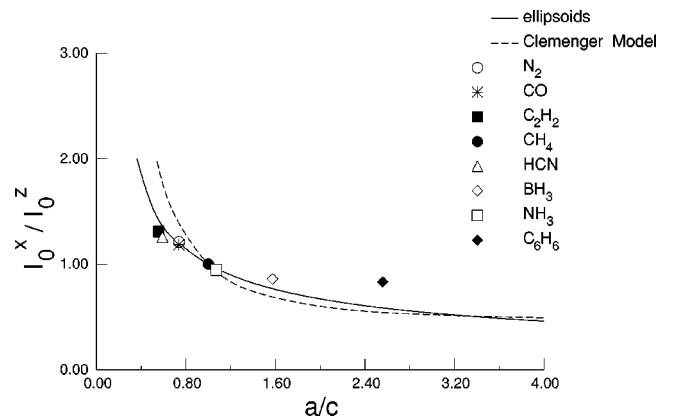


FIG. 2. Directional mean excitation energy ratio as a function of shape for some small molecules. Shapes (spheroidal parameters) are determined from tabulated bond lengths and van der Waals radii; see the text. The specific molecular anisotropies are from polarization propagator calculations [5]. The dashed line is our prediction based on a Clemenger-like model and the full line the result from a jellium based model. Note the improved agreement with the first-principles results; all the points but one are within 10% of the curve from our model.

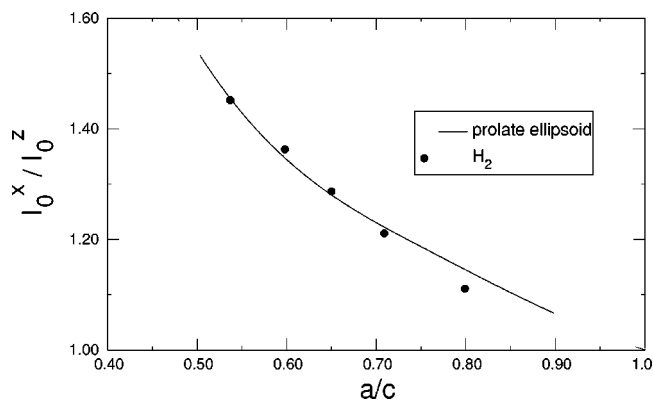


FIG. 3. Directional mean excitation energy ratio as a function of shape for  $H_2$  [30]. The molecular shape again is determined from the bond distance and van der Waals radius. The full curve is our calculation via the modified harmonic oscillator model with input frequencies from a jellium ellipsoid.

ing prolate jellium ellipsoid. The agreement between the molecular data obtained from direct, *ab initio* calculation of directional mean excitation energies and anisotropies obtained indirectly from jellium ellipsoids and simplistic molecular geometrical parameters is remarkable.

Since the curves in Figs. 2 and 3 depend on shape only, any anisotropy in the stopping must arise from geometrical factors only, not from any details of the electronic structure. Thus the geometry of the electron cloud, through its influence on molecular excitation energies, is a major factor in the determination of stopping anisotropy. Certainly if electronic structure anisotropies were included in the curves in Fig. 2, even better agreement with the calculated points would be expected. However, the electrons average out the ionic positions by their motion so that their density distribution is almost unaffected and very well reproduced by a jelliumlike model [10,15]. It should be borne in mind, however,

that the geometry of the molecule indicates only the anisotropy in the energy deposition. The absolute mean excitation energies cannot be predicted with the same level of accuracy directly from molecular geometry. For those, complete dipole oscillator strength distributions are needed for direct calculation or accurate electron density data are needed if the local plasma approximation [17] is to be employed.

Finally, we note that bulk plasmon losses do not appear in our formulation as for small particles most trajectories are nonpenetrating and energy losses are dominated by surface excitations. Furthermore as we split the energy loss into a bulk and a surface part the bulk part is by definition shape independent and drops out of the anisotropy [Eq. (5)].

#### IV. CONCLUSIONS

We have shown, within 10% agreement, that molecular geometry is a good determiner of energy deposition anisotropy. In particular, molecular stopping anisotropy is strongly determined by geometrical anisotropy, molecules are well represented by a harmonic-oscillator model in terms of their stopping anisotropy (the harmonic frequencies taken from a jellium model of the molecules gives the best predictive power); and anisotropy, derived from  $\Delta S(\nu) = S^x(\nu) - S^z(\nu)$  and defined as  $A = \ln(I_0^x/I_0^z)$ , is a function only of the geometrical parameter  $a/c$  (ratio of the minor to the major axis of the ellipsoid describing the molecule in question).

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