Normal modes at small cubes and rectangular particles

1976 J. Phys. A: Math. Gen. 9 627

(http://iopscience.iop.org/0305-4470/9/4/019)

J. Phys. A: Math. Gen., Vol. 9, No. 4, 1976. Printed in Great Britain.

Normal modes at small cubes and rectangular particles

D Langbein

Battelle-Institut e.V., 6 Frankfurt 90, Postfach 900160, Frankfurt/Main, Germany

Received 4 August 1975, in final form 16 December 1975

Abstract. The normal electromagnetic modes at small cubes and rectangular parallelepipeds are discussed. An expansion in terms of external multipoles is used; this allows an analytical evaluation of all elements of the interaction matrix. A cluster point of eigenvalues arises at the eigenvalue $\epsilon_{int}(\omega)+\epsilon_{ext}(\omega)=0$ of a half-space. Only a few terms are needed to obtain convergence of the isolated eigenvalues which give rise to optical absorption peaks. The maximum dipole absorption peak moves from the bulk eigenvalue $\epsilon_{int}(\omega)=0$ to the monopole eigenvalue $\epsilon_{int}(\omega)=-\infty$ with increasing extension of the parallelepiped in the direction of the dipole.

1. Introduction

Small crystals having diameters of only a few angströms usually exhibit a polyhedral habit determined by the lattice structure. It is important to know their normal electric modes in order to understand a number of physical problems such as optical absorption, van der Waals attraction, surface energy, physisorption, chemisorption, and catalysis. Optical absorption at small cubic or rectangular particles has been observed by Martin (1971), Bryskin *et al* (1971), and Genzel and Martin (1972). The van der Waals energy between two particles is given by the change in free energy of their normal electric modes due to their mutual interaction (van Kampen *et al* 1968, Langbein 1974). Physisorption and chemisorption depend on the ability of the normal modes to augment adhesion by virtually or really changing the density of surface electrons (Krupp 1967, Grimley 1967, 1968, Gersten and Tzoar 1974). Similarly, by providing a favourable steric environment and the necessary activation energy, the normal electric modes may strongly enhance a catalytic process.

Normal electric modes at spheres, cylinders, and slabs have been investigated by Englman and Ruppin (1966), Fuchs *et al* (1966), Fuchs and Kliewer (1968), and Englman and Ruppin (1968). Ruppin and Englman (1970) have published a review. On the other hand, only a few results are known on the normal modes at cubes. A paper by van Gelder *et al* (1972) is based on an expansion of the normal modes in terms of spherical harmonics and a numerical evaluation of the resultant interaction terms, followed by the solution of the secular problem for the eigenvalues of the interaction matrix. A different approach has been adopted by Fuchs (1974). He calculates the polarization charges at a set of uniformly distributed points on the surface self-consistently, i.e. in such a manner that the resultant electric field gives rise to the polarization charges. In addition to the eigenfrequencies of the normal modes, Fuchs calculates the dipole components which determine the strength of the absorption peaks.

In the following we consider a small particle of arbitrary geometry. We expand the external potential of a normal electric mode in terms of spherical multipoles. We then calculate the polarization charges induced on the surface of the particle and in turn expand the resultant electric potential in terms of spherical multipoles. We obtain an interaction matrix which is *a priori* diagonal in the case of spheres; its elements can be calculated analytically if rectangular particles are considered. In contrast to the procedure used by van Gelder *et al*, we do not need to integrate the matrix elements numerically, which would appear problematic in view of the magnification of errors involved in the subsequent eigenvalue problem.

We consider all normal modes including not only those exhibiting a dipole component. In the case of a cube there are twenty independent sets of normal modes which belong to ten different symmetry characters (Hund 1956). In the case of a rectangular particle there are eight symmetry characters. We find a cluster point of eigenfrequencies of the normal modes at the eigenfrequency of the normal modes at a half-space. This is because modes exhibiting a high number of zeros can hardly notice the exact shape of the particle. At some distance from the cluster point we find rapid convergence of the eigenfrequencies. Only a few multipoles are needed to derive the main absorption peaks.

The different symmetry characters entail significant deviations in the position of the eigenfrequencies. We obtain a general shift of the eigenfrequencies towards the bulk eigenfrequency if the electric field along a pair of diagonal planes of the cube vanishes. The eigenfrequencies lie altogether between the half-space frequency and the bulk frequency if the electric field vanishes along all diagonal planes. The eigenfrequencies reported by van Gelder *et al* (1972) give rise to some doubt, while those reported by Fuchs (1974) are basically correct on the side of the cluster point distant from the bulk frequency, but show poor accuracy between the half-space frequency and the bulk frequency.

2. Secular system

Let us consider a small particle of arbitrary geometry and dielectric permeability $\epsilon_{int}(\omega)$, which is embedded in a medium of dielectric permeability $\epsilon_{ext}(\omega)$. A normal electric mode of the particle under consideration is obtained if the polarization charge induced by the electric potential $V(\boldsymbol{r})$ in turn causes the potential $V(\boldsymbol{r})$. Using the constitutive equations for the electric field and displacement

$$\boldsymbol{E}(\boldsymbol{r}) = -\nabla V(\boldsymbol{r}); \qquad \boldsymbol{D}(\boldsymbol{r}) = \epsilon(\omega, \boldsymbol{r})\boldsymbol{E}(\boldsymbol{r}) \tag{1}$$

and requiring vanishing divergence of $\boldsymbol{D}(\boldsymbol{r})$ we find

$$\nabla^2 V(\boldsymbol{r}) + \nabla \ln \epsilon(\omega, \boldsymbol{r}) \cdot \nabla V(\boldsymbol{r}) = 0. \tag{2}$$

We obtain a local polarization charge if $\epsilon(\omega, \boldsymbol{r})$ varies spatially. Integrating equation (2) by means of the Green function $|\boldsymbol{r}-\boldsymbol{s}|^{-1}$ yields

$$V(\boldsymbol{r}) = (4\pi)^{-1} \int \mathrm{d}s |\boldsymbol{r}-\boldsymbol{s}|^{-1} \nabla \ln \epsilon(\omega, \boldsymbol{s}) \cdot \nabla V(\boldsymbol{s}) \tag{3}$$

Since $\epsilon(\omega, \boldsymbol{r})$ is assumed constant internally and externally, we find that the integral in equation (3) reduces to a surface integral. Using the surface relation

$$\nabla \ln \epsilon \cdot \nabla V = (-\nabla \epsilon^{-1}) \cdot \epsilon \nabla V = (\epsilon_{int}^{-1} - \epsilon_{ext}^{-1}) \epsilon_{ext} V_{ext} \tag{4}$$

we obtain

$$\gamma V(\boldsymbol{r}) = (4\pi)^{-1} \int_{\text{surf}} \mathrm{d}s |\boldsymbol{r}-\boldsymbol{s}|^{-1} \nabla_n V_{\text{ext}}(\boldsymbol{s}) \tag{5}$$

where

$$\gamma = \epsilon_{\text{int}}/(\epsilon_{\text{ext}} - \epsilon_{\text{int}}). \tag{6}$$

Equation (5) relates the electric potential $V(\boldsymbol{r})$ of a normal mode to the normal component $\nabla_n V_{\text{ext}}(\boldsymbol{r})$ of the external electric field at the surface. Solving equation (5) for the eigenvalues γ yields the eigenfrequencies of the possible normal modes. Van Gelder *et al* transformed equation (5) into a linear secular system by multiplying by $\nabla_n V_{\text{ext}}(\boldsymbol{r})$ and integrating over the surface a second time. However, it is more convenient to expand the external potential and the Green function directly in terms of spherical multipoles. We put

$$V_{\text{ext}}(\boldsymbol{r}) = \sum_{m,\mu} c(m,\mu) r^{-(m+1)} \mathrm{P}_m^{\mu}(\cos\theta) \exp(\mathrm{i}\mu\phi)/(m+\mu)!. \tag{7}$$

Insertion of equation (7) into equation (5), application of the generating series and the addition theorem for Legendre functions, and comparison of the coefficients of the spherical harmonics yields

$$\gamma c(m,\mu) = (m+\mu)! \sum_{n,\nu} c(n,\nu)(4\pi)^{-1} \int_{\text{surf}} \mathrm{d}\boldsymbol{r}\, r'^{n} \mathrm{P}_m^{-\mu}(\cos\theta) \exp(-\mathrm{i}\mu\phi)$$
$$\times \nabla_n [r^{-(n+1)} \mathrm{P}_n^{\nu}(\cos\theta) \exp(\mathrm{i}\nu\phi)/(n+\nu)!]. \tag{8}$$

We have obtained a linear secular system for the eigenvalues γ and the eigenvectors $c(m,\mu)$ of the normal modes. The off-diagonal terms of the interaction matrix are surface integrals over products of spherical multipoles.

Equation (8) can readily be solved in the case of spheres. The choice of spherical multipoles guarantees that the secular matrix (8) is diagonal, and we obtain

$$\gamma = -(m+1)/(2m+1) \tag{9}$$

or

$$m\epsilon_{\text{int}}(\omega) + (m+1)\epsilon_{\text{ext}}(\omega) = 0. \tag{10}$$

This is the well known result reported by Fröhlich (1949) and by Englman and Ruppin (1966).

The electric energy included in the normal modes under investigation is

$$U = (8\pi)^{-1} \int \mathrm{d}\boldsymbol{r}\, \boldsymbol{E}\cdot\boldsymbol{D} = (8\pi)^{-1} \int \mathrm{d}\boldsymbol{r}\, \epsilon \nabla\cdot(V\nabla V). \tag{11}$$

By splitting up the integration in equation (11) into an internal and an external integration and applying Gauss's theorem we find

$$U = (8\pi)^{-1} \epsilon_{\text{int}} \int_{\text{surf}} \mathrm{d}\boldsymbol{r}\, V_{\text{int}} \nabla_n V_{\text{int}} - (8\pi)^{-1} \epsilon_{\text{ext}} \int_{\text{surf}} \mathrm{d}\boldsymbol{r}\, V_{\text{ext}} \nabla_n V_{\text{ext}}. \tag{12}$$

Owing to the continuity of $V(\boldsymbol{r})$ and $\epsilon\nabla_n V(\boldsymbol{r})$ the electric energy built up by the normal modes is found to vanish. The normal modes are self-sustaining, i.e. the electric energy $(8\pi)^{-1}\boldsymbol{E}\cdot\boldsymbol{D}$ necessary to maintain the electric field externally is compensated by an energy gain internally, where $\epsilon_{\text{int}}(\omega) < 0$.

The present investigations are based on the electrostatic limit, which excludes an effective flow of energy. $\epsilon_{\text{int}}(\omega)<0$ means that the modes under investigation are damped exponentially internally, while the ingoing and outgoing flow of energy cancel mutually externally. In this long-wavelength limit no effective absorption is left. In order to find the absorption cross section caused by the normal modes we have to borrow from electrodynamics: the absorption cross section in the long-wavelength limit is given by the amplitude $c(1, 0)$ of the dipole contribution to $V_{\text{ext}}(r)$ according to equation (7) (Mie 1908, Born and Wolf 1959).

3. Separation

The symmetry of the rectangular parallelepiped implies eight different symmetry characters: the normal modes may be even or odd with respect to a reflection at the three central planes $x=0$, $y=0$, and $z=0$. Identifying the polar axis of the spherical multipoles with the z axis of the parallelepiped, we note that only spherical multipoles $P_m^\mu(\cos\theta)\exp(i\mu\phi)$ with even or odd degree m and with even or odd order μ interact. In addition, it is possible to require

$$c(m,-\mu)=\pm c(m,\mu). \tag{13}$$

The resultant eight subdeterminants are conveniently distinguished by the leading multipoles 1, x, y, z, xy, yz, zx, xyz involved. There is one subdeterminant between normal modes which transform like the monopole 1, three subdeterminants between normal modes which transform like the dipoles x, y, z, three subdeterminants between normal modes which transform like the quadrupoles xy, yz, zx, and one subdeterminant between normal modes which transform like the octupole xyz on application of the symmetry operations of the parallelepiped.

The symmetry of the cube gives rise to ten different symmetry characters. The fourfold symmetry around the main axes means that only those spherical multipoles interact whose orders differ by four. This causes a further separation of each of the eight determinants obtained in the case of the parallelepiped into two subdeterminants. The normal modes resulting from the monopole determinant 1 and from the octupole determinant xyz exhibit the full symmetry of the cube even after this separation. The threefold symmetry around the space diagonals thus allows a further separation of the resultant subdeterminants into two. Altogether, we obtain twenty subdeterminants, which represent ten different symmetry characters. Again distinguishing the subdeterminants by the leading multipoles involved we obtain 1, z^2-x^2, z^2-y^2, $(x^2-y^2)(y^2-z^2)(z^2-x^2)$; x, $x(y^2-z^2)$; y, $y(z^2-x^2)$; z, $z(x^2-y^2)$; xy, $xy(x^2-y^2)$; yz, $yz(y^2-z^2)$; zx, $zx(z^2-x^2)$; xyz, $xyz(z^2-x^2)$, $xyz(z^2-y^2)$, $xyz(x^2-y^2)(y^2-z^2)(z^2-x^2)$. The order of the subdeterminants given here reflects their derivation from those obtained in the presence of the parallelepiped. A semicolon indicates that the next subdeterminants of the cube are derived from the subsequent subdeterminant of the parallelepiped.

The interaction of spherical multipoles $P_m^\mu(\cos\theta)\exp(i\mu\phi)$ and $P_n^\nu(\cos\theta)\exp(i\nu\phi)$ with even or odd degree m, n and even or odd order μ, ν only permits an analytical evaluation of all interaction integrals arising in equation (8). The basic integral underlying this integration is the indefinite integral

$$\int dx \int dy\, r^{-3} = z^{-1}\sin^{-1}[xy/(x^2+z^2)^{1/2}(y^2+z^2)^{1/2}] \tag{14}$$

where $r^2=x^2+y^2+z^2$. Equation (14) is easily verified by differentiation with respect to x and y. From equation (14) we obtain all integrals containing a lower power of r by means of the recurrence relation

$$(2n+1)\int dx\int dy\, r^{2n-1}=z^{-1}(d/dz)\int dx\int dy\, r^{2n+1}. \tag{15}$$

The corresponding integrals containing higher powers of r can be written ($n\geqslant 0$)

$$\begin{aligned}(2n+1)\int dx\int dy\, r^{2n-1}&\\ =\sum_{l=0}^{n}&[(2l)!/2^{2l}l!^2]z^{2n-2l}\{x(x^2+z^2)^l\sinh^{-1}[y/(x^2+z^2)^{1/2}]\\ &+y(y^2+z^2)^l\sinh^{-1}[x/(y^2+z^2)^{1/2}]\}\\ &+\sum_{l=0}^{n-1}\sum_{k=l+1}^{n}[(2k)!(k-1)!(k-l-1)!/2^{2l+1}k!(2k-2l)!]\\ &\times z^{2n-2k}xy[(x^2+z^2)^l+(y^2+z^2)^l](x^2+y^2+z^2)^{k-l-\frac{1}{2}}\\ &-z^{2n+1}\sin^{-1}[xy/(x^2+z^2)^{1/2}(y^2+z^2)^{1/2}].\end{aligned} \tag{16}$$

With the integrals over all relevant powers of the radius r being known, we obtain the interaction integrals which contain powers of x^2 and y^2 in addition, by using the recurrence relation

$$(2n+1)\int dx\int dy\, x^{2k+2}y^{2l}r^{2n-1}=[x(d/dx)-(2k+1)]\int dx\int dy\, x^{2k}y^{2l}r^{2n+1}. \tag{17}$$

The number of terms necessary for an explicit representation of the surface integrals (8) is generally rather high owing to the number of terms included in the Legendre polynomials $P_m^{\mu}(\cos\theta)$ and $P_n^{\nu}(\cos\theta)$ and the number of terms arising by repeated application of recurrence relations (15) and (17). Collecting these terms is a typical computer task.

4. Convergence

In order to demonstrate the convergence of the present procedure, in table 1 we give the leading terms of the monopole subdeterminant 1 and of the dipole subdeterminant z resulting in the case of the cube. In setting up the monopole subdeterminant 1 we used the interdependence of the coefficients $c(2m, 4\mu)$ of multipoles of equal degree $2m$ according to

$$\sum_{\mu}\left[\binom{2l}{l-2\mu}-\frac{(-1)^m}{2^{2m-4l}}\binom{2m-2l}{m-l-2\mu}\right]c(2m,4\mu)=0 \tag{18}$$

$l=0,\ldots,[\frac{1}{2}m]$, which results from the threefold symmetry around the space diagonals. We note from table 1 that the eigenvalue corresponding to the monopole, $\gamma=-1$, is maintained in each order of the interaction. $\gamma=-1$ also represents the eigenvalue of the monopole in the presence of a sphere. However, the monopole mode is now coupled to a 2^4-pole, 2^6-pole, etc. The coupling is strongest in the case of the 2^4-pole

Table 1. Monopole and dipole subdeterminants.

$(m, \mu; n, \nu)$	(0, 0)	(4, 0)	(6, 0)	(8, 0)	(10, 0)	
(0, 0)	1	0	0	0	0	
(4, 0)	−0·665391 E+1	0·591608 E+0	−0·208230 E−2	−0·371047 E−5	0·108360 E−7	
(6, 0)	0·801871 E+5	−0·186527 E+1	0·666480 E+0	−0·134700 E−3	−0·172704 E−5	
(8, 0)	0·214169 E+5	−0·334615 E+3	0·443186 E+0	0·541045 E+0	−0·905390 E−4	
(10, 0)	−0·258470 E+7	0·495942 E+5	−0·266761 E+4	−0·152694 E+1	0·579652 E+0	
$(m, \mu; n, \nu)$	(1, 0)	(3, 0)	(5, 0)	(7, 0)	(5, 4)	(7, 4)
(1, 0)	0·666667 E+0	−0·136131 E−1	−0·141803 E−4	0·728842 E−6	0·787793 E−5	0·154603 E−6
(3, 0)	−0·136316 E+1	0·513520 E+0	0·663637 E−3	0·666569 E−5	0·603674 E−3	−0·304886 E−6
(5, 0)	−0·703790 E+1	0·177512 E+1	0·532663 E+0	−0·675572 E−3	−0·106352 E−1	−0·197794 E−5
(7, 0)	0·227706 E+4	−0·242891 E+2	−0·412855 E+1	0·519759 E+0	−0·995031 E+0	−0·185289 E−1
(5, 4)	−0·838129 E+2	0·115394 E+2	−0·134004 E+0	−0·757631 E−3	0·628805 E+0	0·973712 E−3
(7, 4)	0·780236 E+3	0·182284 E+3	−0·143554 E+1	−0·873505 E−1	0·243326 E+1	0·590093 E+0

and decreases rapidly with increasing degree of the poles. The eigenvalue corresponding to the unperturbed dipole $P_1(\cos\theta)$ is $\gamma=-2/3$, which once more equals the eigenvalue of the dipole in the presence of a sphere. The dipole mode is now coupled to the octupole $P_3(\cos\theta)$ and to two 2^5-poles and thus is shifted towards the monopole eigenvalue -1. The strongest coupling is that to the octupole.

The product of corresponding off-diagonal elements $(m, \mu; n, \nu)$ and $(n, \nu; m, \mu)$ in the subdeterminants shown in table 1 is generally small compared with the product of the diagonal elements $(m, \mu; m, \mu)$ and $(n, \nu; n, \nu)$. This guarantees rapid convergence and permits perturbation theory to be applied to all isolated eigenvalues. Since the diagonal elements in all subdeterminants exhibit a cluster point at $\gamma=-0{\cdot}5$, which is the eigenvalue of the normal modes at a half-space, we expect the convergence of the eigenvalues to improve with increasing distance from the half-space eigenvalue.

The development of the eigenvalue spectrum, if multipoles of increasing degree are taken into account, is shown in figure 1. The upper part of figure 1 corresponds to the monopole subdeterminant 1, the lower part to the dipole subdeterminant z. The full lines at the left represent the eigenvalues of the unperturbed monopole and dipole, respectively. The unperturbed eigenvalues of the next multipoles to be considered are indicated by dotted lines. If the coupling to these multipoles is taken into account, we obtain the eigenvalue spectrum shown in the next column, and so on. We find an increasing number of eigenvalues to split off from the cluster point and note a rapid convergence of these isolated levels. In order to obtain the outer dipole levels with reasonable accuracy, it is sufficient to take into account the nine multipoles (1, 0), (3, 0), (5, 0), (5, 4), (7, 0), (7, 4), (9, 0), (9, 4), and (9, 8). The next inner eigenvalues converge satisfactorily if the multipoles (11, 0), (11, 4), (11, 8), (13, 0), (13, 4), (13, 8), and (13, 12) are considered as well. Similar observations are made if the eigenvalues resulting from the other subdeterminants are considered.

5. Cubes

In figure 2 we exhibit the complete eigenvalue spectrum of the normal electric modes at a cube. Multipoles up to degree 13 are taken into account. This means that the secular determinants under consideration have orders between two and sixteen. For each set of eigenvalues the symmetry of the respective normal modes and the degeneracy are indicated. The accuracy of all levels increases with increasing distance from the cluster point $\gamma=-0{\cdot}5$.

The different symmetry characters entail several corresponding differences in the eigenvalue spectra. The non-degenerate normal modes, which behave like 1 and xyz, cause eigenvalues confined to the region $-0{\cdot}5\geqslant\gamma\geqslant-1$. This is also the region of the eigenvalues found in the case of spheres, which are shown at the right-hand side. From a comparison of the level spectra shown at the left and at the right it appears that the eigenvalues in the case of the cube approach the cluster point according to a reciprocal law similar to that described by equation (9). The levels resulting from subdeterminant 1 approximately satisfy $\gamma\simeq(m+1{\cdot}6)/(2m+1{\cdot}6)$.

The normal modes $(x^2-y^2)(y^2-z^2)(z^2-x^2)$ and $xyz(x^2-y^2)(y^2-z^2)(z^2-x^2)$, which have been separated from modes 1 and xyz on account of the threefold symmetry around the space diagonals, cause eigenvalues which are confined to the region $-0{\cdot}5\leqslant\gamma\leqslant0$. These modes show a vanishing electric field along the diagonal planes of the cube, i.e. they are mainly localized within the cube. The principle of equal internal

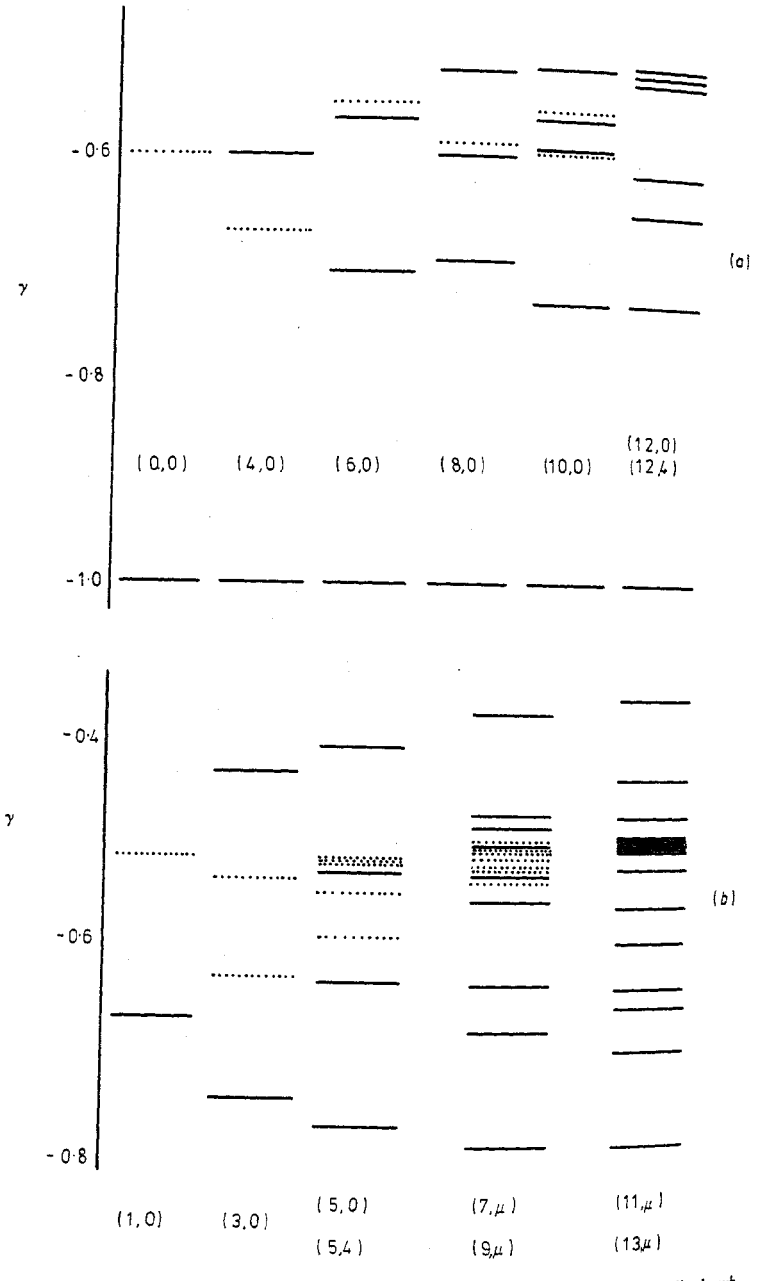


Figure 1. Convergence of eigenvalues. (*a*) monopole subdeterminant 1; (*b*) dipole subdeterminant *z*.

and external electric energy discussed in § 2 means that a small internal dielectric permeability $\epsilon_{\text{int}}(\omega)$ is sufficient.

The normal modes corresponding to the remaining symmetry characters yield eigenvalues both below and above the cluster point $-0{\cdot}5$. We may distinguish between two different groups. The modes behaving like z, xy, and xyz cause similar eigenvalue

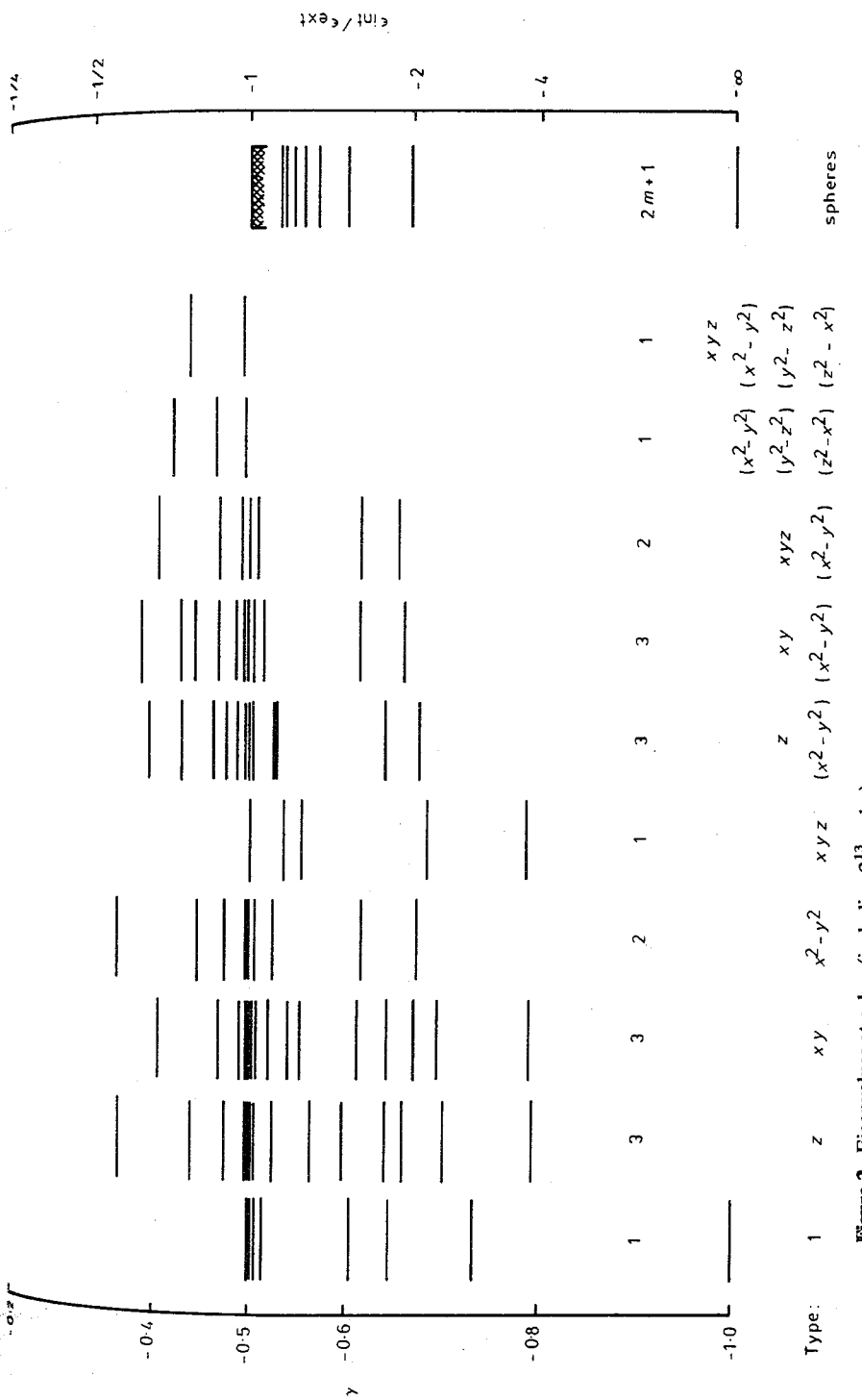


Figure 2. Eigenvalues at cubes (including 2^{13}-poles).

spectra; these are slightly shifted towards $\gamma = -0{\cdot}5$ if the minimum degree of the spherical harmonics considered increases. A second set of similar eigenvalue spectra is due to the modes behaving like (x^2-y^2), $z(x^2-y^2)$, $xy(x^2-y^2)$, and $xyz(x^2-y^2)$. Whereas changing the parity with respect to the middle planes $x=0$, $y=0$, $z=0$ merely results in a small shift of the eigenvalues, a large shift is observed if the parity is changed with respect to the diagonal planes $x=\pm y$, $y=\pm z$, $z=\pm x$.

For reasons outlined in § 2 we judge the strength of the dipole absorption peaks by the relative amplitude $c(1, 0)$ of the dipole $P_1(\cos\theta)$. From the rapid convergence of the eigenvalue spectrum shown in figure 1 we conclude that only a few of the outer eigenvalues can exhibit a dipole contribution worth mentioning. The dipole absorption peaks at $\gamma = -0{\cdot}793$, $-0{\cdot}702$, $-0{\cdot}660$, $-0{\cdot}363$ are found to have the relative weights $0{\cdot}60, 0{\cdot}10, 0{\cdot}05, 0{\cdot}25$, respectively. The remaining relative weight $0{\cdot}05$ is spread over the rest of eigenvalues. This is illustrated in figure 3.

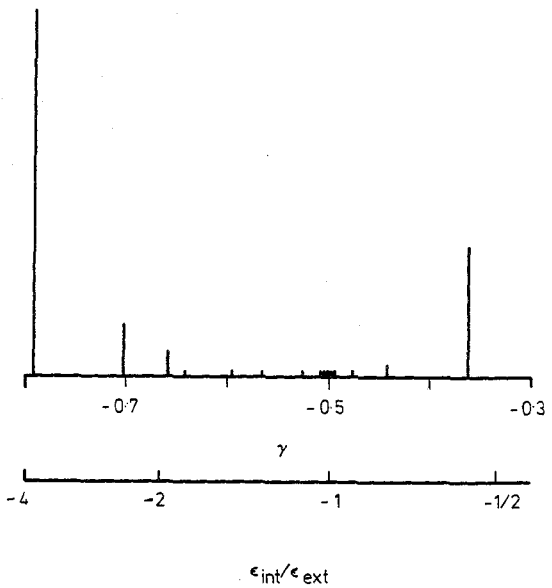


Figure 3. Dipole absorption peaks.

In table 2 we compare the findings on the dipole modes according to the investigations discussed here with those obtained by van Gelder *et al* (1972) and Fuchs (1974). Van Gelder *et al* calculate the eigenvalue α, which is related to γ according to $\gamma = \alpha/4\pi - 1$. Fuchs calculates the eigenvalue ϵ, from which we obtain γ according to $\gamma = \epsilon/(1-\epsilon)$. We include the findings based on the nine spherical multipoles $(1, 0)$ to $(9, 8)$ and those based on the sixteen spherical multipoles $(1, 0)$ to $(13, 12)$. The eigenvalues reported by van Gelder *et al*, which were also obtained by taking into account the nine spherical multipoles $(1, 0)$ to $(9, 8)$, show poor agreement with the results reported by Fuchs and of our own investigations. It is noted that one eigenvalue is split off on each side of the cluster point. However, the position of these eigenvalues is less accurate than that resulting from the present procedure if only two spherical multipoles are taken into account. The findings by Fuchs obtained by optimizing the polarization charge at 57 non-equivalent points on the surface of the cube agree very

Table 2. Comparison of dipole eigenvalues.

van Gelder *et al* (1972) $\gamma=\alpha/4\pi-1$	Fuchs (1974) $\gamma=\epsilon/(1-\epsilon)$	Present paper	
		(1, 0) to (9, 8)	(1, 0) to (13, 12)
−0·710	−0·786	−0·785	−0·793
−0·569	−0·703	−0·681	−0·702
−0·525	−0·655	−0·637	−0·660
			−0·642
−0·519	−0·559	−0·555	−0·597
			−0·566
−0·507		−0·532	−0·527
−0·504		−0·503	cluster point
−0·500		−0·487	−0·477
−0·491	−0·438	−0·473	−0·442
−0·442	−0·296	−0·377	−0·363

well with our own findings in the region $\gamma<-0{\cdot}5$; agreement is less satisfactory for $\gamma>-0{\cdot}5$. This suggests that the normal modes which are mainly localized within the cube are not sufficiently sensitive to variations in the surface polarization charge.

6. Rectangular parallelepipeds

The transition from a cube to a rectangular parallelepiped implies a systematic variation of the surface integrals in secular system (8). The only integrals which are not changed are those containing the monopole (0, 0). The diagonal element (0, 0; 0, 0) equals −1, the off-diagonal elements (0, 0; n, ν) equal 0. This means that the monopole mode always has the eigenvalue $\gamma=-1$ or $\epsilon_{int}/\epsilon_{ext}=-\infty$. The monopole is coupled to the multipoles, but this does not affect its eigenvalue.

All diagonal elements (m, μ; m, μ) in the secular system (8) are limited to the region between the value 0 corresponding to low external fields and the monopole value −1 corresponding to high external fields. For a parallelepiped with extensions X, Y, Z, the dipole term (1, 0; 1, 0) equals

$$-(2/\pi)\tan^{-1}[Z(X^2+Y^2+Z^2)^{1/2}/XY]. \tag{19}$$

It approaches the value −1 if the extension along the direction of the dipole becomes large so that the energy of the external field must be compensated by the localized energy gain at the small bases of the parallelepiped, and the value 0 if the extension normal to the direction of the dipole becomes large so that the total volume contributes to the internal energy gain. The quadrupole term (2, 0; 2, 0) equals

$$-1+\frac{3}{\pi}\frac{XYZ[1/(X^2+Z^2)+1/(Y^2+Z^2)]}{(X^2+Y^2+Z^2)^{1/2}}. \tag{20}$$

It approaches −1, if the extension of the parallelepiped in one direction becomes much smaller than that in the other directions.

With increasing degree m we find that the diagonal elements (m, μ; m, μ) in the secular system (8) approach the limiting value −0·5. The value of the surface integral in the case of a half-space is its cluster point for any given extension X, Y, Z of the

parallelepiped. The shape of the particle under investigation merely affects the rate of the approach to the cluster point. This means that the accuracy of the eigenvalues obtained by means of the procedure discussed here increases with increasing distance from the cluster point $\gamma = -0{\cdot}5$, but decreases when the shape of the particle becomes more irregular.

The explicit eigenvalue spectrum obtained by taking into account all spherical harmonics up to degree 10 is shown in figures 4 to 8. Figure 4 exhibits the sequence according to which the different spectra have been arranged. We compare parallelepipeds with equal base and increasing height. The parallelepipeds denoted by P1 to P5 have a quadratic base. This sequence represents the transition from a slab to a cube and a rod. The indices P6 to P9 and P10 to P12 denote parallelepipeds with the rectangular bases 0·4, 1 and 0·1, 1, respectively.

In figure 5 we depict the eigenvalues resulting from subdeterminant 1. The respective normal modes exhibit the full symmetry of the parallelepiped. They are coupled to the monopole mode, but do not have a monopole component themselves. If one pair of faces of the parallelepiped is quadratic, they can be subdivided into modes which acquire a factor $+1$ or -1 on rotation by $\frac{1}{2}\pi$ around the tetragonal axis. The eigenvalues corresponding to the symmetry character -1 are denoted by broken lines. They can be seen to increase with increasing height Z of the parallelepiped in the sequence P1 to P5, whereas the eigenvalues corresponding to the symmetry character

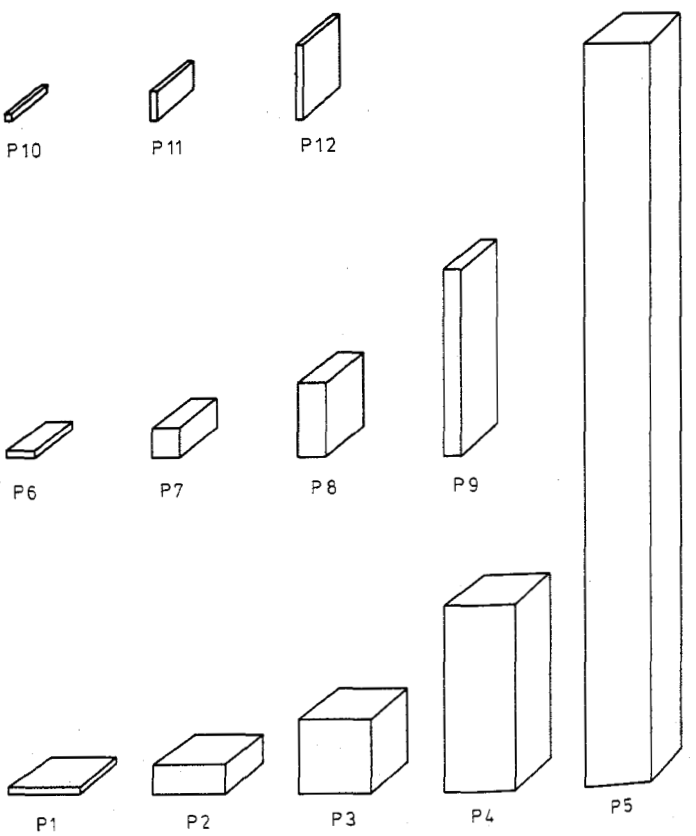


Figure 4. Sequence of parallelepipeds.

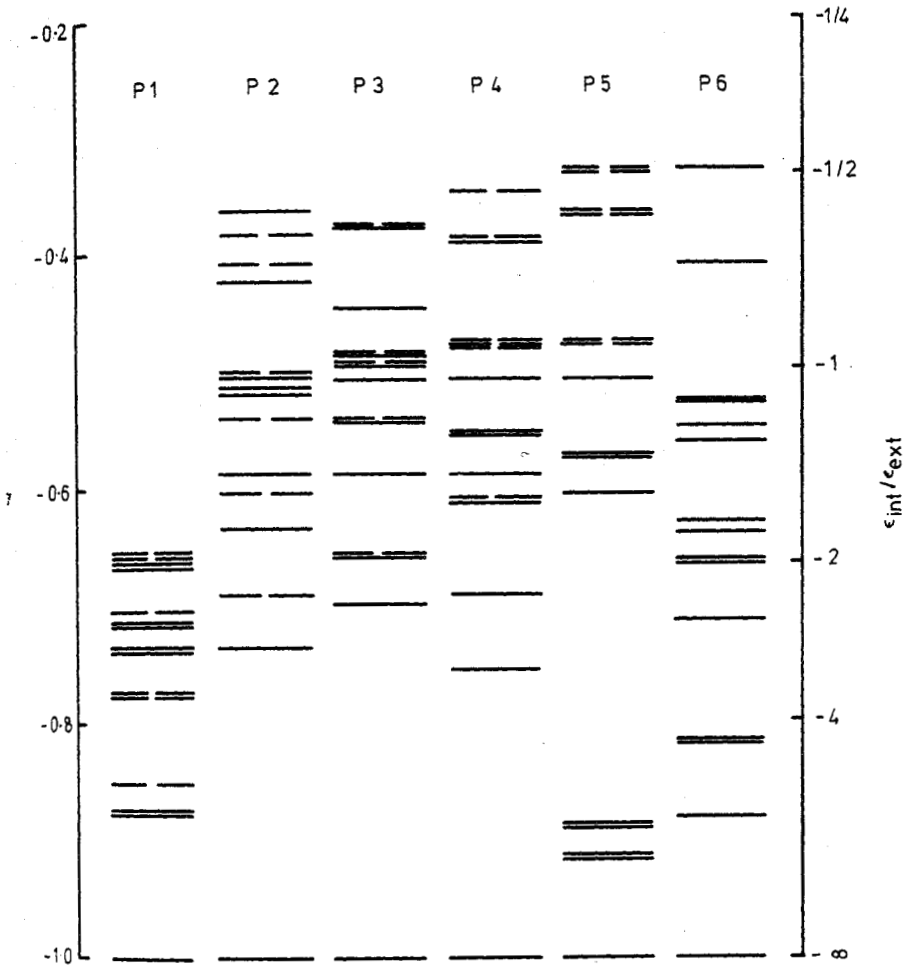
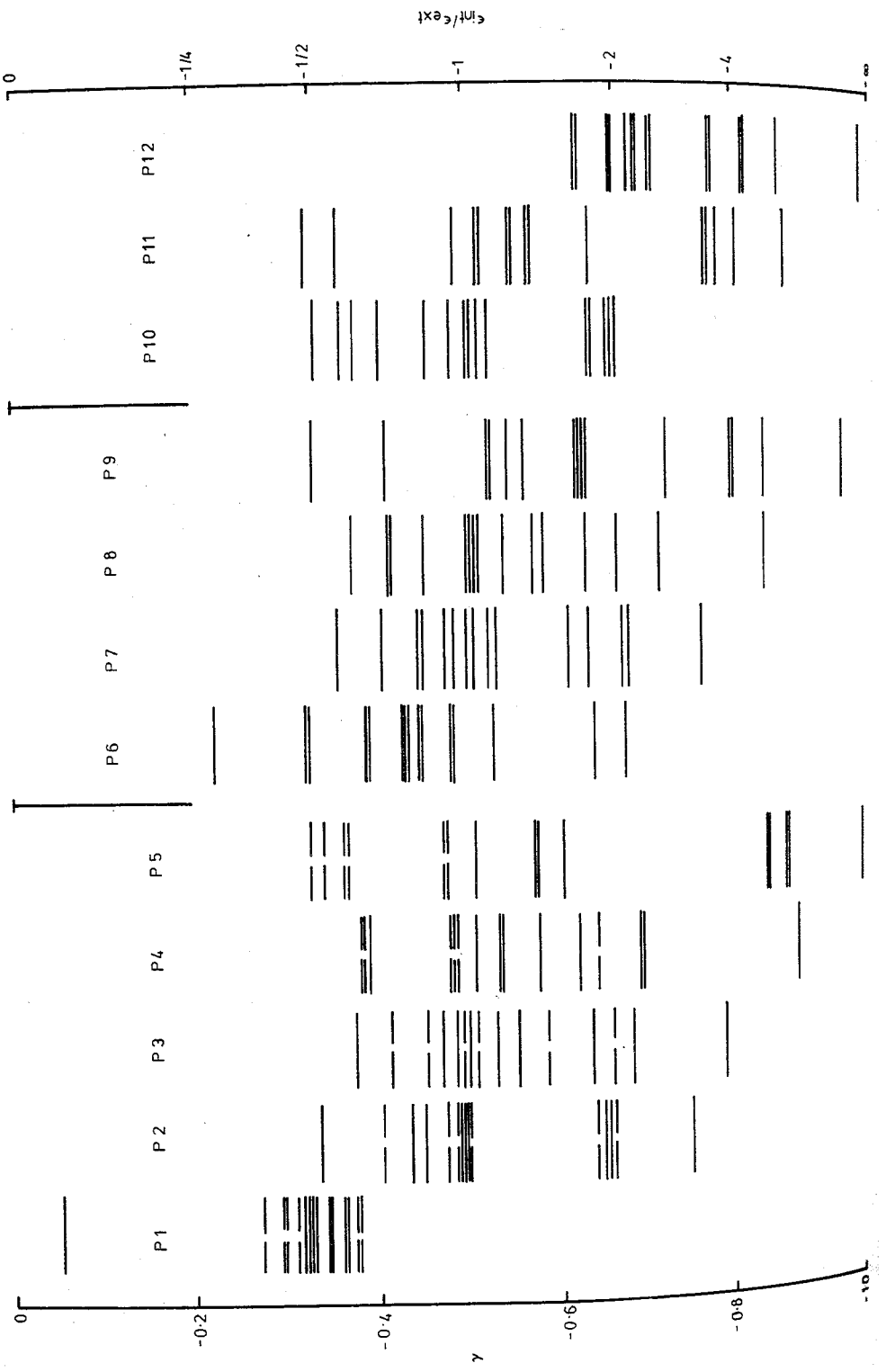


Figure 5. Monopole eigenvalues.

+1 have a maximum in the case of the cube P3. In the case of the rod P5, the two level spectra are fully separated. The levels corresponding to -1 lie above $\gamma = -0{\cdot}5$, those corresponding to $+1$ lie below $\gamma = -0{\cdot}5$. We found a similar separation of level spectra in the case of the cube.

In figure 6 the dipole eigenvalues resulting from subdeterminants x, y, and z are plotted. We have turned the direction of all dipoles to the z direction and have changed the orientation of the parallelepiped accordingly. Within each of the sequences P1 to P5, P6 to P9, and P10 to P12 we find a tendency of the eigenvalues to approach -1 with increasing height Z. This agrees with the tendency of the diagonal element (1, 0; 1, 0) according to equation (19). However, because of the cluster point at $-0{\cdot}5$, the highest dipole eigenvalue is merely shifted from 0 to $-0{\cdot}5$ and the lowest dipole eigenvalue is merely shifted from $-0{\cdot}5$ to -1. This shift of eigenvalues with increasing height becomes less pronounced as the base of the parallelepiped becomes more elongated. The eigenvalue exhibiting maximum dipole absorption strength essentially follows the behaviour of the diagonal element (1, 0; 1, 0), i.e. it moves from 0 to -1 with increasing height Z.


$\epsilon_{int}/\epsilon_{ext}$
0
-1/4
-1/2
-1
-2
-4
-∞
P12
P11
P10
P9
P8
P7
P6
P5
P4
P3
P2
P1
0
-0·2
-0·4
-0·6
-0·8
-1·0
γ

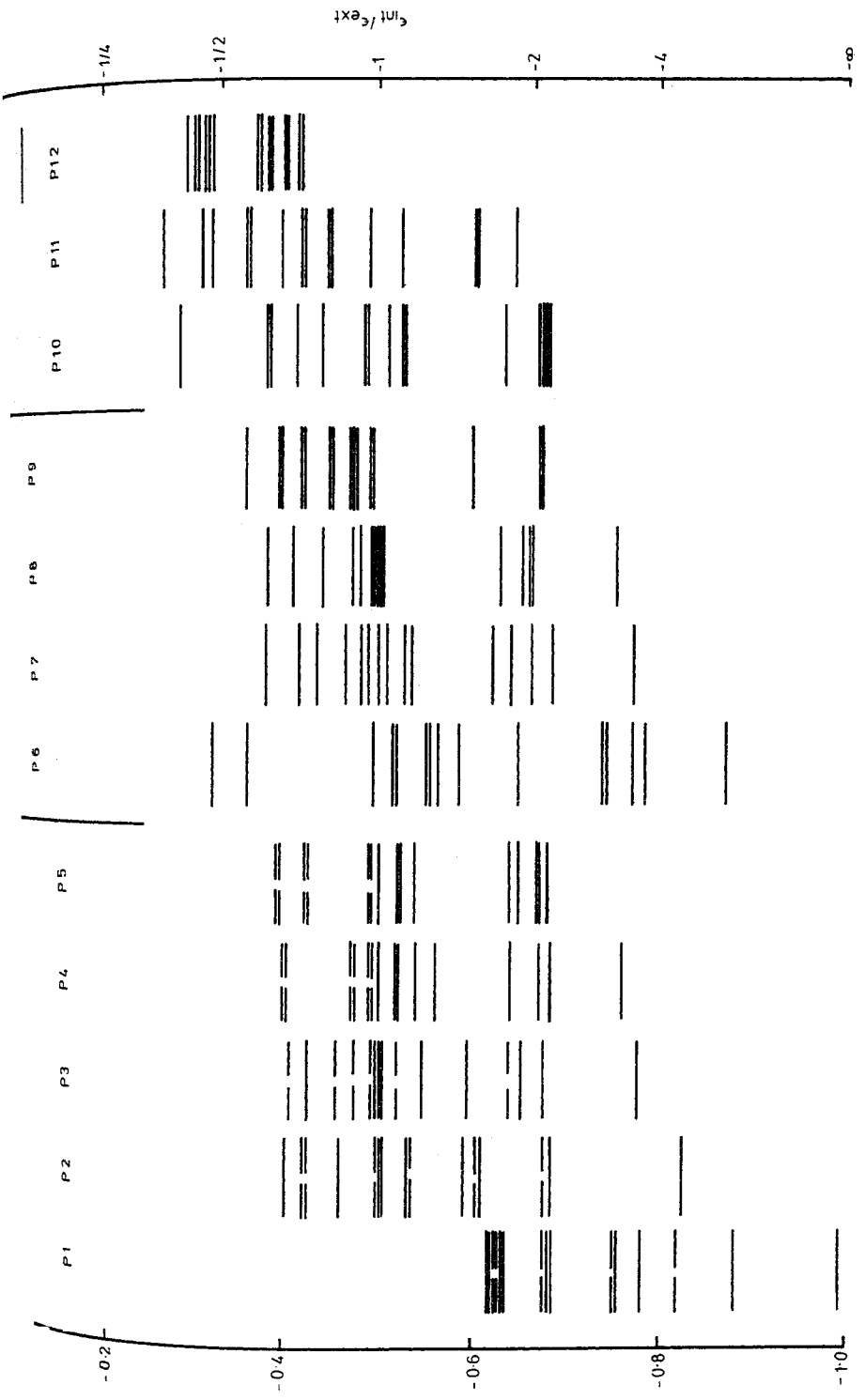


Figure 7. Quadrupole eigenvalues.

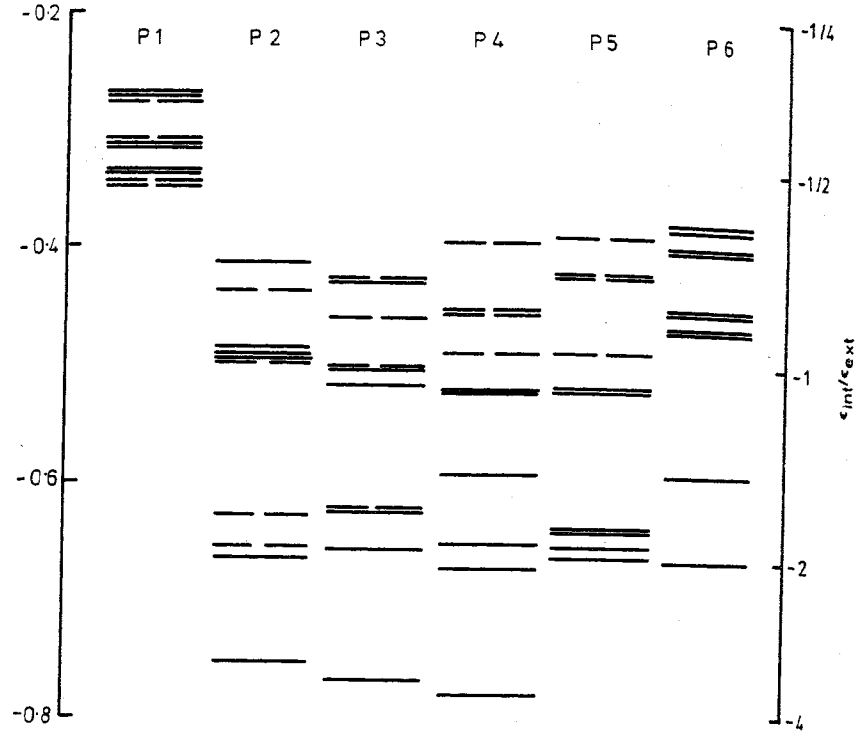


Figure 8. Octupole eigenvalues.

The fact that in the vicinity of the cluster point $-0{\cdot}5$ no eigenvalues at all are obtained for some elongated shapes may be attributed to the slow convergence of the diagonal elements to the cluster point in these cases. If the base of the parallelepiped is quadratic, i.e. in the sequence P1 to P5, it is again possible to distinguish between modes which acquire a factor $+1$ or -1 on rotation by $\frac{1}{2}\pi$ around the tetragonal axis. The eigenvalues corresponding to the latter symmetry character have zero dipole absorption strength. They are essentially octupoles and show a minimum as a function of the height Z rather than a monotonic decrease.

The findings obtained for monopole and dipole modes hold in an analogous manner also for quadrupole and octupole modes. The quadrupole eigenvalues resulting from secular determinants xy, yz, and zx have a tendency to increase with increasing height Z of the parallelepiped, as does the quadrupole diagonal element (2, 0; 2, 0) according to equation (20). Roughly, we may consider the quadrupole and octupole eigenvalue spectra as inversions of the dipole and monopole eigenvalue spectra at the cluster point $-0{\cdot}5$.

7. Conclusions

We have presented a rapidly convergent method, which renders the normal electromagnetic modes at a small rectangular particle within a minimum of computer time. The overall trend of the eigenvalues may even be obtained without using a computer.

All elements of the interaction matrix between the multipoles under consideration can be calculated analytically. Although this generally requires a large number of polynomial terms, only a few terms are left in the leading diagonal elements which cause the main absorption peaks.

All eigenvalues of the normal modes are necessarily confined to the region $0 \geqslant \gamma \geqslant -1$ which corresponds to the region $0 \geqslant \epsilon_{int}/\epsilon_{ext} \geqslant -\infty$. The internal and the external dielectric permeabilities must have opposite signs so that the energy needed to build up the external electric field is made up by an internal energy gain, or *vice versa.* The main dipole absorption peak may be shifted through the full region $0 \geqslant \gamma \geqslant -1$ by changing the extensions of the parallelepiped. A short extension in the direction of the dipole favours an eigenvalue close to 0. In that case there is relatively little interaction left between the polarization charges on the faces normal to the direction of the dipole so that changing the sign in some distant regions hardly affects the resulting eigenvalues and nearly degenerate eigenvalues arise. The main quadrupole eigenvalue in the case of the upright slab P12 lies very close to the main dipole eigenvalue in the case of the horizontal slab P1. Similar to the case of spheres we find a cluster point of eigenvalues at the half-space value $-0{\cdot}5$. However, the eigenvalues close to the cluster point do not give rise to optical absorption peaks. Their dipole component is generally very small.

The cube is the most probable shape of small rectangular particles. It has the advantage that it needs the minimum number of spherical harmonics to provide convergence, and its symmetry allows a further reduction of the resultant secular determinants. We find only small deviations between the eigenvalue spectra corresponding to the symmetry characters z, xy, and xyz, which again indicates that there is only little interaction between polarization charges at distant surface regions of the cube. On the other hand, there arises a strong effect on the eigenvalue spectra if the normal modes exhibit an additional factor x^2-y^2. This factor means that the electric field vanishes along the diagonal planes $x=\pm y$, which reduces the energy of the external multipole fields and shifts the eigenvalue spectra towards 0. If the normal modes exhibit the factor $(x^2-y^2)(y^2-z^2)(z^2-x^2)$, i.e. if the electric field vanishes along all diagonal planes, we find the eigenvalue spectra fully confined to the region between the bulk value $\gamma=0$ and the half-space value $\gamma=-0{\cdot}5$.

Acknowledgments

This study was sponsored by Battelle Institute, Columbus, Ohio, under Grant Number 333-302.

References

Born M and Wolf E 1959 *Principles of Optics* (London, New York, Paris, Los Angeles: Pergamon) § 13.5
Bryskin V V, Gerbstein Y M and Mirlin D W 1971 *Solid St. Commun.* **9** 669
Englman R and Ruppin R 1966 *Phys. Rev. Lett.* **16** 898
—1968 *J. Phys. C: Solid St. Phys.* **1** 1515
Fröhlich H 1949 *Theory of Dielectrics* (Oxford: Clarendon) p 149
Fuchs R 1974 *Phys. Lett.* **48A** 353
Fuchs R and Kliewer K L 1968 *J Opt. Soc. Am.* **58** 319
Fuchs R, Kliewer K L and Pardee W J 1966 *Phys. Rev.* **150** 589
van Gelder A P, Holvast J, Stoelinga J H and Wyder P 1972 *J. Phys. C: Solid St. Phys.* **5** 2757

Genzel L and Martin T P 1972 *Phys. Stat. Solidi* (b) **51** 101
Gersten J I and Tzoar N 1974 *Solid St. Commun.* **15** 425
Grimley T B 1967 *Proc. Phys. Soc.* **92** 776
—— 1968 *Am. Chem. Soc.* **90** 3016
Hund F 1956 *Handb. Phys.* **36** 1 (Berlin: Springer)
van Kampen N G, Nijboer B R A and Schram K 1968 *Phys. Lett.* **26A** 307
Krupp H 1967 *Adv. Colloid Interface Sci.* **1** 111
Langbein D 1974 *Springer Tracts in Modern Physics* vol 72 (Berlin: Springer) p 1
Martin T P 1971 *Solid St. Commun.* **9** 623
Mie G 1908 *Ann. Phys., Lpz* **25** 377
Ruppin R and Englman R 1970 *Rep. Prog. Phys.* **33** 149