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1977 J. Phys. A: Math. Gen. 10 1031

(http://iopscience.iop.org/0305-4470/10/6/022)

J. Phys. A: Math. Gen., Vol. 10, No. 6, 1977. Printed in Great Britain.

Normal electric modes at small polyhedral particles

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Received 5 October 1976, in final form 7 December 1976

Abstract. The electric potential of a normal mode at a dielectric or metallic polyhedron is expanded in terms of spherical multipoles. By inducing surface charges each multipole induces secondary multipoles. It is shown that all matrix elements of the resultant secular problem can be calculated analytically, which considerably improves convergence of the eigenvalues of the normal modes. The total shift of eigenvalues caused by multipoles of equal degree is proved to be independent of the shape of the polyhedron under consideration. Simple recurrence relations for separating the secular problem in the case of tetrahedral or cubic symmetry are derived and explicit eigenvalue schemes for some standard polyhedrons are given.

1. Introduction

We recently reported a new method of calculating the normal electric modes at cubes and rectangular particles (Langbein 1976). By expanding the electric potential of the normal modes in terms of spherical multipole potentials we calculated the polarization charges induced on the surface of the particle under investigation, and in turn expanded the electric potential caused by the polarization charges in terms of spherical multipoles. This self-consistent approach has the advantage that all matrix elements between the primary and induced multipoles can be integrated analytically. Compared to earlier papers on normal electric modes at cubes (van Gelder *et al* 1972, Fuchs 1974) the convergence of the eigenvalues of the normal modes is improved considerably. The number of multipoles required to achieve comparable accuracy is reduced by a factor of five.

In this paper we extend the investigations on the normal modes at small particles to cover polyhedrons of arbitrary shape. We derive a set of recurrence relations, from which all relevant surface integrals can be calculated, and prove the conservation law that the mean position of all eigenvalues is independent of the shape of the polyhedron. Turning to polyhedrons with tetrahedral or cubic symmetry we substitute cubic harmonics for the spherical harmonics and calculate explicit eigenvalue schemes for a series of usual habits.

2. Secular system

The basic idea underlying the calculation of the normal electric modes at a small dielectric particle was described in a recent paper (Langbein 1976). The external

electric potential $V(\boldsymbol{r})$ of a normal mode is expanded in terms of spherical multipoles, the polarization charges induced at the surface of the particle are calculated, and the resulting secondary potential is again expanded in terms of spherical multipoles. Self-consistency means that the primary and the induced potential are identical. Putting externally

$$V(\boldsymbol{r}) = \sum_{m,\mu} c(m,\mu) r^{-(m+1)} P_m^{\mu}(\cos\theta) \exp(\mathrm{i}\mu\phi)/(m+\mu)! \tag{1}$$

we obtain the secular system

$$\gamma c(m,\mu) = (m+\mu)! \sum_{n,\nu} c(n,\nu)(4\pi)^{-1} \int_{\text{surf}} \mathrm{d}\boldsymbol{r}\, r^m P_m^{-\mu}(\cos\theta) \exp(-\mathrm{i}\mu\phi)$$
$$\times \nabla_{\text{norm}}[r^{-(n+1)} P_n^{\nu}(\cos\theta) \exp(\mathrm{i}\nu\phi)/(n+\nu)!] \tag{2}$$

where γ is the eigenvalue containing the internal and the external dielectric functions $\epsilon_{\text{int}}(\omega)$ and $\epsilon_{\text{ext}}(\omega)$,

$$\gamma = \epsilon_{\text{int}}(\omega)/(\epsilon_{\text{ext}}(\omega) - \epsilon_{\text{int}}(\omega)). \tag{3}$$

The integration in equation (2) extends over the surface of the particle, the derivative ∇_{norm} is to be taken normal to the surface. The integers m, n and μ, ν run over degree and order of the multipole potentials under consideration.

The evaluation of the surface integrals in equation (2), in the presence of a polyhedron of arbitrary shape, involves two major steps. The first step is to rotate the polar axis of the multipoles under consideration to the normal vectors pointing from the centre of the polyhedron to its different faces. The second step covers the integration on the different faces.

The first step is based on the rules of coordinate transformations. We denote the coordinate normal to a particular face of the polyhedron by z and the angle between the z axis and the polar axis of the spherical multipoles by α (see figure 1). Then we choose the x axis to be perpendicular to one of the edges of the face considered. The Eulerian angle between the x axis and the axis of rotation is denoted by β and that between the zero azimuth axis and the axis of rotation by ψ (see figure 1). Hence

$$r\cos\theta = (-x\sin\beta + y\cos\beta)\sin\alpha + z\cos\alpha$$
$$r\sin\theta\exp(\mathrm{i}\phi) \tag{4}$$
$$= \{(x\cos\beta + y\sin\beta) + \mathrm{i}[(-x\sin\beta + y\cos\beta)\cos\alpha - z\sin\alpha]\exp(\mathrm{i}\psi)\}.$$

In order to perform the integration over a particular face it is convenient to dissect the face into right triangles. We connect the point of intersection of the z axis with all corners and draw the heights with respect to all edges (see figure 2). This yields $2N$ triangles, where N is the number of edges. We denote the lengths of the heights by u_i and the sections on the edges by v_i ($i = 1, 2, \ldots, 2N$)(see figure 2).

Rotating the x axis successively into the direction of all heights leaves us with integrations over the standard triangle shown in figure 3. The integrand is a polynomial in x and y and may contain positive or negative powers of the distance

$$r = (x^2 + y^2 + z^2)^{1/2}. \tag{5}$$

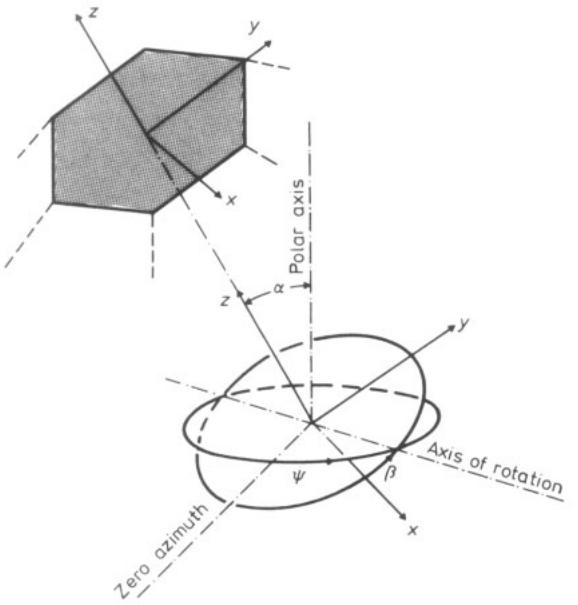

Figure 1. Rotation of coordinates.

We thus have to deal with the surface integrals

$$\int_{\text{surf}} \mathrm{d}\boldsymbol{r}\, x^k y^l r^m \equiv \int_0^u \mathrm{d}x \int_0^{vx/u} \mathrm{d}y\, x^k y^l (x^2+y^2+z^2)^{m/2}. \tag{6}$$

The surface integrals (6) can be evaluated analytically for arbitrary powers k, l and m of x, y and z. If the polyhedron has a centre of inversion, there is no interaction between multipoles of even and odd degree, so that we are interested in odd powers of m only.

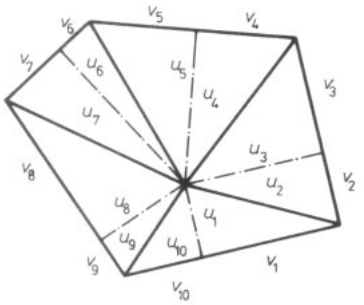

Figure 2. Dissection of faces.

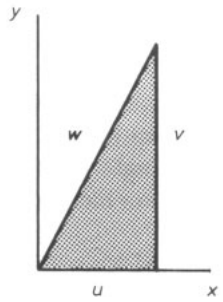

Figure 3. Standard triangle.

The surface integrals (6) are easily evaluated by means of a few recurrence relations. The most obvious recurrence relation results directly from equation (5):

$$\iint \mathrm{d}x\, \mathrm{d}y\, x^{k+2} y^l r^m + \iint \mathrm{d}x\, \mathrm{d}y\, x^k y^{l+2} r^m + z^2 \iint \mathrm{d}x\, \mathrm{d}y\, x^k y^l r^m = \iint \mathrm{d}x\, \mathrm{d}y\, x^k y^l r^{m+2}. \tag{7}$$

Two further recurrence relations between the surface integrals (6) are obtained by

partial integration with respect to x and y. Taking appropriate linear combinations of the resulting equations yields

$$(k+l+m+2)\iint \mathrm{d}x\ \mathrm{d}y\, x^k y^l r^m - mz^2 \iint \mathrm{d}x\ \mathrm{d}y\, x^k y^l r^{m-2}$$
$$= u^{k+1} \int_0^v \mathrm{d}y\, y^l (u^2+y^2+z^2)^{m/2} \tag{8}$$

$$m\iint \mathrm{d}x\ \mathrm{d}y\, x^k y^{l+2} r^{m-2} + (l+1)\iint \mathrm{d}x\ \mathrm{d}y\, x^k y^l r^m$$
$$= (v/u)^{l+1} \int_0^u \mathrm{d}x\, x^{k+l+1} [x^2(1+v^2/u^2)+z^2]^{m/2}. \tag{9}$$

By means of equations (8) and (9) we can lower or raise m and k, respectively. Lowering or raising l is achieved by also using equation (7). Equations (7)–(9) lower or raise k, l, and m by two, i.e. as initial values of the surface integrals we need

$$\iint \mathrm{d}x\ \mathrm{d}y\, r^{-3} = z^{-1} \tan^{-1}[uv/(r_u^2 + zr_w)] \tag{10}$$

$$\iint \mathrm{d}x\ \mathrm{d}y\, xr^{-3} = (v/w)\sinh^{-1}(w/z) - \sinh^{-1}(v/r_u) \tag{11}$$

$$\iint \mathrm{d}x\ \mathrm{d}y\, yr^{-3} = \sinh^{-1}(u/z) - (u/w)\sinh^{-1}(w/z) \tag{12}$$

$$\iint \mathrm{d}x\ \mathrm{d}y\, xyr^{-3} = (r_u - z) - (u/w)^2 (r_w - z) \tag{13}$$

where

$$w = (u^2+v^2)^{1/2}, \qquad r_u = (z^2+u^2)^{1/2}, \qquad r_w = (z^2+w^2)^{1/2} \tag{14}$$

are, respectively, the hypotenuse of the right triangle under consideration and the distances of its edges from the centre.

The single integrals over x and y in equations (8) and (9) and their recurrence relations are elementary.

3. Eigenvalue conservation

Before explicitly calculating the dependence of the eigenvalues γ on the shape of a particular polyhedron, let us state that the sum over all eigenvalues does not depend on the shape of the polyhedron at all. More explicitly, we shall prove that the total shift of the eigenvalues caused by spherical multipoles of equal degree m and different order μ is independent of the shape of the polyhedron considered. Among the consequences of this conservation law we find that the monopole eigenvalue always equals -1 and that the Lorentz–Lorenz relation holds for all polyhedrons exhibiting three independent equivalent space directions.

Using the fact that the sum over all eigenvalues γ equals the trace of the secular matrix (2), we now consider those contributions to the trace which result from multipoles of equal degree m and varying order μ. By summing the diagonal terms in equation (2) over μ and partial integration we have

$$\sum_{\mu=-m}^{+m}(4\pi)^{-1}\int_{\text{surf}}\mathrm{d}r\,r^m P_m^{-\mu}(\cos\theta)\exp(-\mathrm{i}\mu\phi)\nabla_{\text{norm}}[r^{-(m+1)}P_m^{\mu}(\cos\theta)\exp(\mathrm{i}\mu\phi)]$$

$$=(4\pi)^{-1}\int_{\text{surf}}\mathrm{d}r\Big(r^{2m}\sum_{\mu}P_m^{-\mu}(\cos\theta)P_m^{\mu}(\cos\theta)\nabla_{\text{norm}}r^{-(2m+1)}$$

$$+r^{-(2m+1)}\tfrac{1}{2}\nabla_{\text{norm}}r^{2m}\sum_{\mu}P_m^{-\mu}(\cos\theta)P_m(\cos\theta)\Big). \tag{15}$$

The two sums over μ on the right-hand side of equation (15) are identical and equal 1, as can be seen from the addition theorem for Legendre functions (Erdélyi *et al* 1953, equation 3.11.(2)). The normal gradient ∇_{norm} thus applies to the distance r only. By commutation of r^{2m} and $r^{-(2m+1)}$ with ∇_{norm} we find that the right-hand side of equation (15) turns into $(m+1)$ times the surface integral over the electric flux through the polyhedron. Independent of the shape of the polyhedron we obtain

$$\sum_{\mu=-m}^{+m}(4\pi)^{-1}\int_{\text{surf}}\mathrm{d}r\,r^m P_m^{-\mu}(\cos\theta)\exp(-\mathrm{i}\mu\phi)\nabla_{\text{norm}}[r^{-(m+1)}P_m^{\mu}(\cos\theta)\exp(\mathrm{i}\mu\phi)]$$

$$=-(m+1). \tag{16}$$

The contribution of the $(2m+1)$ spherical multipoles of equal degree m and varying order μ to the trace of the secular matrix (2) equals $-(m+1)$. In the case of spheres, where these $(2m+1)$ multipoles are equivalent, the contribution of each multipole equals $-(m+1)/(2m+1)$, yielding the well known result $\gamma=-(m+1)/(2m+1)$.

In the case of polyhedrons we learn from equation (16) that the contribution of the monopole $m=\mu=0$ to the trace of the secular matrix equals -1. This is also the eigenvalue corresponding to the monopole mode, since all matrix elements between the monopole $m=0$ and the multipoles $n\neq 0$ vanish. Whereas the monopole generally induces surface charges, which couple it to multipoles, the multipoles do not in turn give rise to a monopole.

The three dipoles $m=1$, $\mu=-1$, 0, $+1$ are equivalent, whenever the polyhedron under consideration exhibits three independent equivalent axes. The contribution of each dipole to the trace of the secular matrix (2) then equals $-\frac{2}{3}$, i.e. the secondary dipole induced by a primary dipole equals that arising in the case of spheres. This means validity of the Lorentz–Lorenz relation. However, the reservation has to be made that a primary dipole does not only induce a secondary dipole but also secondary multipoles which give rise to additional tertiary dipoles, so that we have to cope with correction terms of the order of $(\epsilon_{\text{ext}}(\omega)-\epsilon_{\text{int}}(\omega))^2$.

If the polyhedron under consideration is extended in one direction, the contribution of the corresponding dipole to the trace of the secular matrix (2) increases, whereas the contribution of the two other dipoles decreases by half that amount according to equation (16). The conservation principle of eigenvalues thus easily explains many of the findings on normal modes at rectangular particles reported by Langbein (1976).

4. Cubic harmonics

The solution of the secular problem (2) can usually be greatly simplified by applying group theoretical arguments. The spherical multipole potentials used in equation (1) are fully adapted to the symmetry of the sphere. The secular system resulting in this case is diagonal. In order to separate satisfactorily the secular system arising in the presence of a polyhedron we have to adapt the multipole potentials to the irreducible representations of the symmetry group of the polyhedron. Since in the following we are interested in polyhedrons exhibiting tetrahedral or octahedral symmetry, we demonstrate this adaptation at the point group O_h of the regular octahedron. The group O_h gives rise to ten different representations. These are up to threefold degenerate, so that altogether twenty sets of adapted multipole potentials result. We need at least one set of potentials corresponding to each representation.

The linear combinations of spherical harmonics adapted to the point group O_h are called cubic harmonics. They were introduced by van der Lage and Bethe (1947). The cubic harmonics are also adapted to the group T_d of the regular tetrahedron, but fewer matrix elements in equation (2) vanish in that case. Tables representing the cubic harmonics in terms of spherical harmonics have been reported by Altmann and Cracknell (1965) and up to degree 30 by Muggli (1972). These tables usually give the expansion coefficients of the cubic harmonics in terms of the normalized spherical harmonics. The expansion coefficients become integers if an expansion in terms of the un-normalized spherical harmonics used in equation (1) is considered instead. In the following we present explicit recurrence relations for these integer coefficients, which are well suited to be used within a computer program.

We identify the polar axis of the spherical multipoles (1) with one of the fourfold axes of the octahedron (with the z axis), so that only multipoles interact whose orders μ, ν differ by a multiple of four. The reflections at the symmetry planes $x = 0$, $y = 0$, $z = 0$, in addition, entail that there is no interaction between multipoles with even and odd degree and between the real and the imaginary parts. Using the selection rules

$$m + n \equiv 0 (\mathrm{mod}\ 2), \qquad \mu + \nu \equiv 0 (\mathrm{mod}\ 4), \qquad c(m, -\mu) = \pm c(m, \mu) \tag{17}$$

we find the secular system (2) to separate into 16 independent secular systems. The secular matrices arising for $\mu \equiv 1, 3 (\mathrm{mod}\ 4)$ are equivalent to those arising for $\mu \equiv 0, 2 (\mathrm{mod}\ 4)$, $c(m, -\mu) = (-1)^{m+1} c(m, \mu)$. These are the four irreducible representations Γ_4, Γ_4', Γ_5, and Γ_5' having a degeneracy of three.

The remaining four secular matrices can be further separated, each into two. They yield the irreducible representations with degeneracy 1 or 2. A convenient way of finding these representations is to expand symmetrically the spherical multipoles in terms of the rectangular coordinates x, y, z. Then, requiring parity ± 1 on any interchange of two coordinates renders the representations with degeneracy 1, whereas requiring the sum over all permutations of the three coordinates to vanish renders the representations with degeneracy 2.

For $m \equiv 0 (\mathrm{mod}\ 2)$, $c(m, -\mu) = +c(m, \mu)$ only even powers $x^{2r} y^{2s} z^{2t}$ with $2r + 2s + 2t = m$ arise, yielding

$\Gamma_1 : m \equiv 0 (\mathrm{mod}\ 2), \mu \equiv 0 (\mathrm{mod}\ 4), c(m, -\mu) = +c(m, \mu)$

$$\mathrm{parity}\left[(-1)^t 2^{2t} \sum_{\mu} c(m, \mu) \sum_{l} (-1)^l \binom{2r}{r + l + \frac{1}{2}\mu} \binom{2s}{s + l} \right] = +1 \tag{18}$$

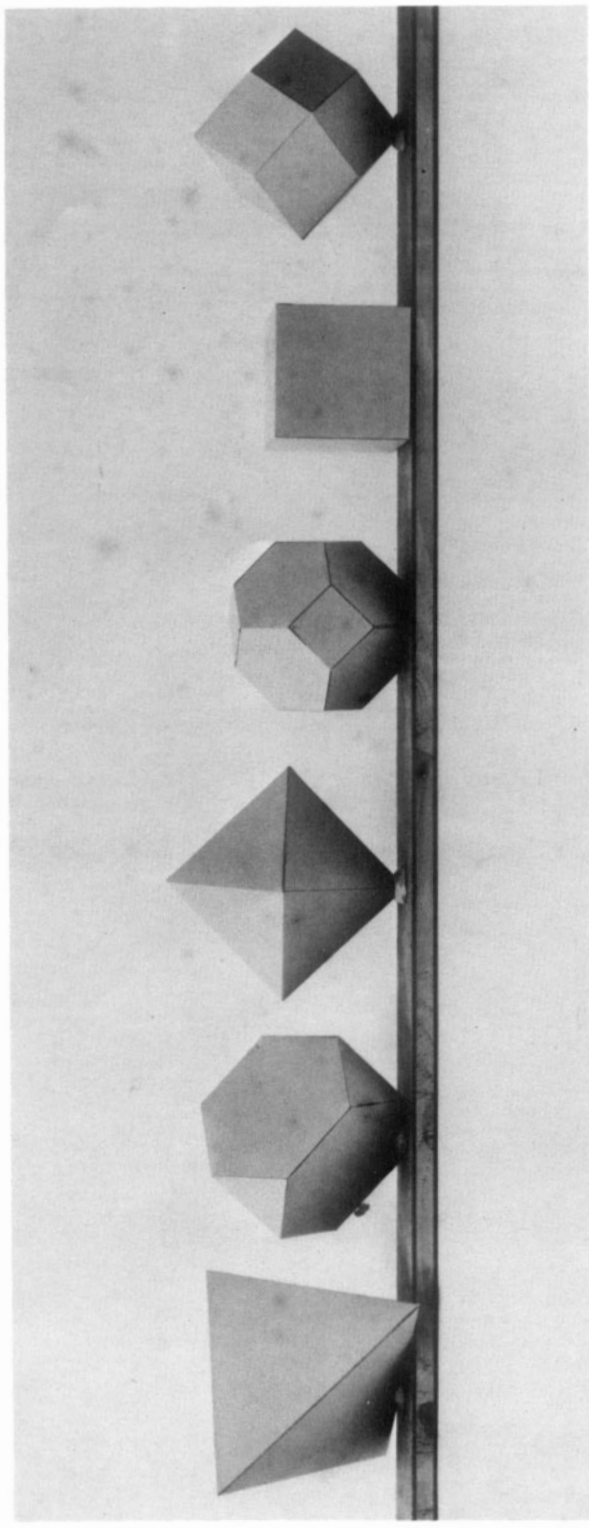

Figure 4. Hab its with tetrahedral and c bic symmetry.

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on any interchange of two parameters r, s, t.

$\Gamma_2 : m \equiv 0 (\mathrm{mod}\ 2),\ \mu \equiv 2 (\mathrm{mod}\ 4),\ c(m,-\mu) = +c(m,\mu)$

$$\mathrm{parity}\left[(-1)^t 2^{2t} \sum_{\mu} c(m,\mu) \sum_{l} (-1)^l \binom{2r}{r+l+\frac{1}{2}\mu} \binom{2s}{s+l}\right] = -1 \tag{19}$$

on any interchange of two parameters r, s, t.

$\Gamma_3 : m \equiv 0 (\mathrm{mod}\ 2),\ \mu \equiv 0 (\mathrm{mod}\ 4),\ c(m,-\mu) = +c(m,\mu)$

$$\sum_{P} (-1)^t 2^{2t} \sum_{\mu} c(m,\mu) \sum_{l} (-1)^l \binom{2r}{r+l+\frac{1}{2}\mu} \binom{2s}{s+l} = 0 \tag{20}$$

where the first sum runs over all permutations $P(r, s, t)$ of the three parameters r, s, t.

For $m \equiv 1 (\mathrm{mod}\ 2)$, $c(m,-\mu) = -c(m,\mu)$ only odd powers $x^{2r+1} y^{2s+1} z^{2t+1}$ with $(2r+1)+(2s+1)+(2t+1) = m$ are left, yielding the representations Γ_2', Γ_1', Γ_3'. The recurrence relations for the coefficients $c(m,\mu)$ corresponding to these representations result from equations (19)–(21) by substituting $(2r+1)$, $(2s+1)$, $(2t+1)$, and $(2l-1)$ for $2r$, $2s$, $2t$, and $2l$.

Usually, several of the recurrence relations arising for different parameters r, s, t are linearly dependent. For example, in order to obtain all independent recurrence relations for the coefficients of the representation Γ_1 it is sufficient to consider relation (18) for $s = 0$ only.

5. Numerical results

Figure 4 shows a number of polyhedrons exhibiting tetrahedral or cubic symmetry, which are usual habits of small single crystals. In the order chosen in figure 4 they result from each other by systematically cutting off the corners. Let us begin with the tetrahedron at the left. Cutting off corner segments at one third of the edges causes the original faces to become regular hexagons, while the new faces are regular triangles. Let us call this polyhedron a curtailed tetrahedron. If larger corner segments of the tetrahedron are cut off, so that the edges are cut at one half rather than at one third, an octahedron is obtained. Now cutting off corner segments of the octahedron at one third of the edges yields the cuboctahedron, which is the Wigner–Seitz cell of the body-centered cubic lattice. Cutting off corner segments of the octahedron at one half rather than at one third of the edges yields the cube. Finally, by cutting off edge segments of the cube up to the middle of the faces, we obtain the rhombohedron, which is the Wigner–Seitz cell of the face-centered cubic lattice.

Figures 5–9 exhibit the eigenvalues of the normal electric modes resulting in the case of the six above polyhedrons. In the case of tetrahedral symmetry there exist five irreducible representations, each of which splits into two when cubic symmetry is approached. The two cubic representations merging to the same tetrahedral representation are shown in the same figure. They are distinguished by full lines (representations Γ) and broken lines (representations Γ').

The left-hand sides of figures 5–9 result by taking into account spherical multipoles up to degree 4, whereas in the eigenvalue schemes shown at the right-hand side spherical multipoles up to degree 6 are included. The inclusion of multipoles of increasing degree mainly increases the number of eigenvalues close to the cluster point

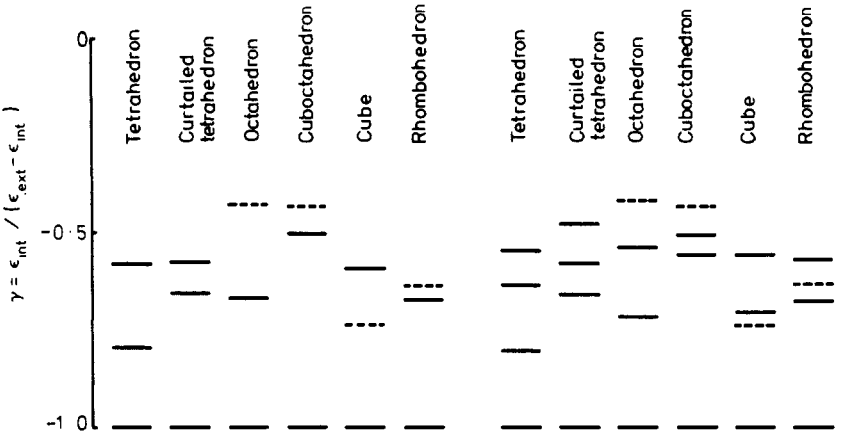

Figure 5. Type 1, xyz; representation Γ_1, Γ_2'; degeneracy 1.

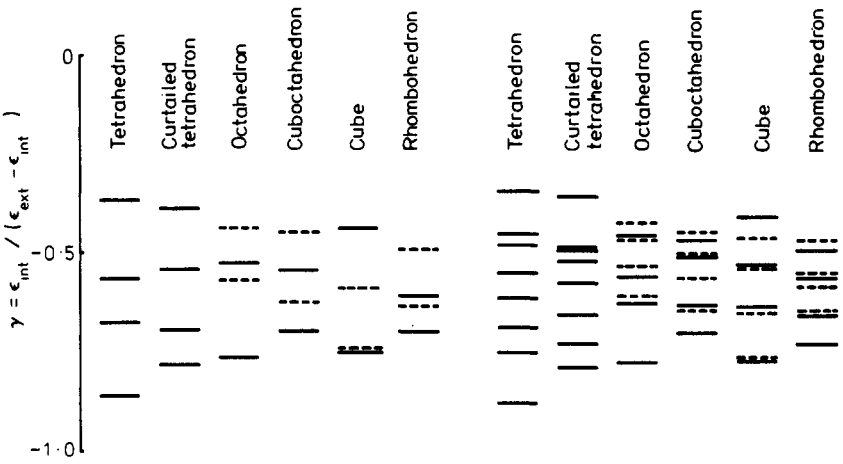

Figure 6. Type z, xy; representation Γ_5, Γ_4'; degeneracy 3.

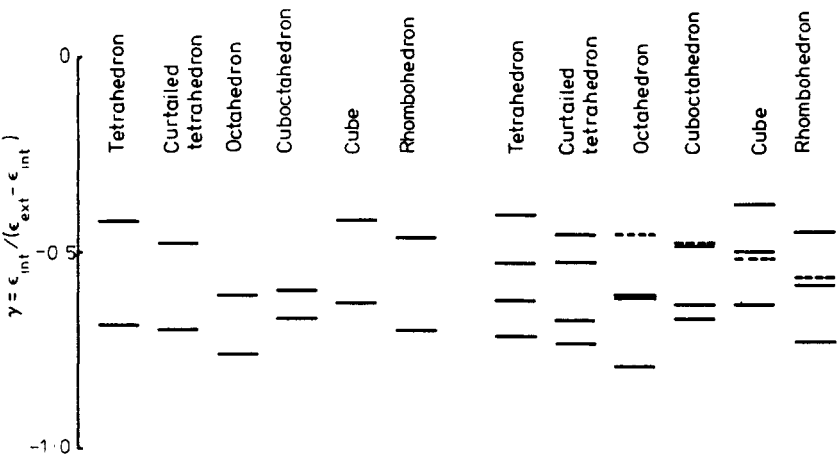

Figure 7. Type (x^2-y^2), $xyz(x^2-y^2)$; representation Γ_3, Γ_3'; degeneracy 2.

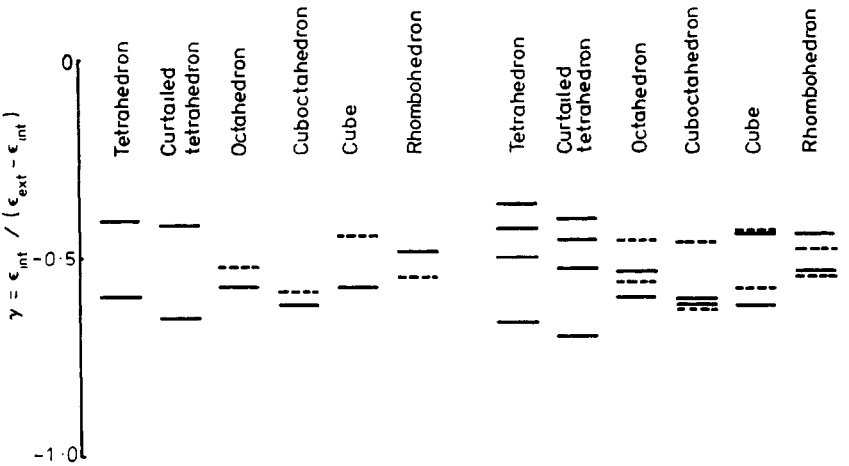

Figure 8. Type $z(x^2-y^2)$, $xy(x^2-y^2)$; representation Γ_4, Γ_5'; degeneracy 3.

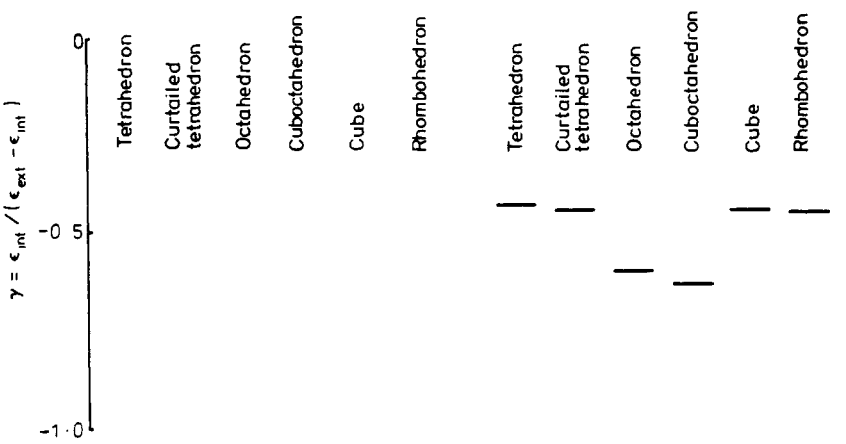

Figure 9. Type $(x^2-y^2)(y^2-z^2)(z^2-x^2)$, $xyz(x^2-y^2)(y^2-z^2)(z^2-x^2)$; representation Γ_2, Γ_1'; degeneracy 1.

$\gamma = -0{\cdot}5$, which is the eigenvalue of the normal electric modes at a half-space. The obvious reason for this cluster point is the fact that multipoles of high degree exhibit a large number of nodes: their wavelength at the surface decreases with increasing degree.

The appearance of all additional eigenvalues close to the cluster point $\gamma = -0{\cdot}5$ entails that the isolated eigenvalues caused by the multipoles of low degree are slowly shifted towards the eigenvalue $\gamma = 0$ of the normal electric modes in an infinite medium or towards the eigenvalue $\gamma = -1$ of the monopole mode. The convergence of these eigenvalues is very rapid. Except for the appearance of new levels close to $-0{\cdot}5$, there are only minor differences between the eigenvalue schemes obtained by including multipoles up to degree 4 or 6.

Figure 5 shows the normal modes belonging to the representations Γ_1 and Γ_2'. They have parity $+1$ on an interchange of two coordinates x, y, z. We have stated already in § 3, that the monopole eigenvalue always equals -1. In the case of the four polyhedrons

exhibiting cubic symmetry, all eigenvalues belonging to the representation Γ_1 turn out to be confined to the region $-0{\cdot}5 \geq \gamma \geq -1$. This result has been shown to hold in the presence of a cube even if multipoles up to degree 13 are included (Langbein 1976). The levels denoted by broken lines belong to the representation Γ_2'. These levels also appear at one side of the cluster point only. It is always the side opposite to that where the levels belonging to the representation Γ_2 appear (see figure 9).

Figure 6 gives the normal modes belonging to the representations Γ_5 and Γ_4'. They are threefold degenerate. Within the electrostatic (or long-wavelength) limit under investigation, only the modes belonging to Γ_5 give rise to dipole scattering and absorption. The cross section for dipole scattering by the different modes is roughly given by the relative contribution of the multipoles of degree $m = 1$. In general, this cross section is found to be higher for the isolated eigenvalues than for those close to the cluster point. However, it depends characteristically on the polyhedron under consideration, whether the eigenvalues close to 0 or close to -1 cause the strongest dipole scattering. The tetrahedron and the curtailed tetrahedron give rise to strong dipole scattering above the cluster point ($0 \geq \gamma \geq -0{\cdot}5$). The octahedron and the rhombohedron show about equally strong scattering on both sides of the cluster point, the total cross section of the octahedron being larger than that of the rhombohedron. The cuboctahedron and the cube cause a strong dipole scattering for the isolated eigenvalues below the cluster point ($-0{\cdot}5 \geq \gamma \geq -1$).

Figures 7–9 refer to the representations requiring higher degrees of the multipoles. The fact that no levels at all appear on the left-hand side of figure 9 is due to the inclusion of multipoles of degrees 4 and 6 only.

6. Conclusions

Small particles of only a few ångströms diameter usually take a polyhedral habit which is determined by the lattice structure. Frequently one finds a habit given by the Wigner–Seitz cell, but various other shapes have also been observed (Uyeda 1975). In order to interpret the absorption and scattering spectra of these particles, their normal electric modes must be known. We have shown that the rapidly convergent method originally set up for finding the normal modes at cubes can be applied to polyhedrons of arbitrary shapes. All necessary surface integrals can be calculated analytically; the respective recurrence relations and initial values are given. This enables a straightforward computer calculation of all normal modes.

It is shown that the total shift of eigenvalues caused by the $(2m+1)$ multipoles of equal degree is independent of the shape of the polyhedron considered. As a consequence, the monopole eigenvalue always equals -1 and the Lorentz–Lorenz relation holds for all polyhedrons exhibiting three equivalent space directions. A systematic shift of the cross section for dipole scattering from γ-values above $-0{\cdot}5$ to γ-values below $-0{\cdot}5$ (from ϵ-values above -1 to ϵ-values below -1) is found when the shape of the polyhedron changes from a tetrahedron to a cube. More detailed investigations into the dipole scattering and absorption cross sections require application of the electrodynamic rather than the electrostatic limit. This will be reported in a subsequent paper.

Knowledge of the normal electric modes at polyhedral particles is important not only for an understanding of optical absorption and various surface phenomena, but also in investigations on voids in dielectrics or metals. Such voids, too, usually show a

polyhedral habit and are included in the present procedure by the interchange of $\epsilon_{int}(\omega)$ and $\epsilon_{ext}(\omega)$. Another promising application is the calculation of lattice structures in van der Waals crystals like those of the inert gases. The difference in binding energy between the FCC and the HCP structures is so small that the usual van der Waals type calculations may favour another structure depending on the number of multiplet contributions included. Investigations based on normal electric modes eliminate this difficulty by accounting for all multiplet interactions from the start.

Perhaps the most promising application of the present method is to the calculation of the habits of small particles itself. The total free energy corresponding to a distinct habit is determined by the zero-point energy of the electromagnetic radiation field. The present method permits convergent investigations on the change in zero-point energy relative to that resulting for spherical shape. From the conservation law for the eigenvalues we conclude that the total zero-point energy of the radiation field would not depend on the shape of the particle at all, if the eigen-frequencies ω were proportional to the eigenvalues γ, i.e. $\epsilon_{int}/\epsilon_{ext} = c(\omega - \omega_0)/[1 + c(\omega - \omega_0)]$, where c is an arbitrary constant. The deviations of $\epsilon_{int}(\omega)$ from this simplified behaviour determine the habit with lowest free energy. With increasing particle size, when the long-wavelength limit is no longer applicable, so that the scattering and absorption cross sections depend characteristically on the wavelength and retardation effects become important, the particle shape exhibiting lowest energy may change. For substances exhibiting plasma resonances in the usual range of a few electron volts, this change in shape is expected at sizes of the order of magnitude of 0·1 μm.

Acknowledgments

This study was supported by Battelle Institute, Columbus, Ohio, under Grant Number 333-315. The author acknowledges several most stimulating discussions with his experimental partner Matthias Selders.

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