STATIC DIELECTRIC PROPERTIES OF AN ENSEMBLE OF RESTRICTED ONE-DIMENSIONAL OSCILLATORS

by

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CONTENTS

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I. ABSTRACT

Deviations from constancy of the Clausius-Mossotti function, C_M with changes in density and temperature are considered on the basis of a one-dimensional oscillator model of the atom in which the valence electrons are assumed restricted by infinite potentials, but interact with all others in the medium through dipolar forces.

The density-dependence of C_M is qualitatively in agreement with experiment, but the temperature-dependence is negligible as the excited states of an oscillator do not represent those of real atoms. In addition, the model does not permit the existence of the ionized state of the atom.

The analysis here suggest a more promising, three-dimensional model which admits of realistic atomic potentials, dipolar interaction based on continuous dielectric surroundings and repulsive potentials which ensure the existence of delocalized electronic states with consequent screening of the dipolar forces.

II. INTRODUCTION, BACKGROUND AND SUMMARY

It is well known for nonpolar materials that the static permittivity ε_s obeys fairly well the Clausius-Mossotti formula:

$$\frac{\varepsilon_s-1}{\varepsilon_s+2} = \frac{4\pi}{3} N_o \alpha_o \tag{II:1}$$

where N_o is the particle number density and α_o is the polarizability of the isolated atom or molecule being considered. Since $N_o = \rho A/W$ where ρ is the mass density, W the molecular weight and $A = 6.02\text{x}10^{23}$ is Avogadro's number, (II:1) indicates for a given nonpolar material that the Clausius-Mossotti function:[†]

$$C_M = \frac{W}{\rho}\left(\frac{\varepsilon_s-1}{\varepsilon_s+2}\right) = \left(\frac{4\pi A}{3}\right)\alpha_o \tag{II:2}$$

should be a constant independent of density and temperature. C_M should also be independent of frequency up to the point where appreciable optical absorption by the material begins to occur, usually in the infrared region.

[†] In the literature C_M is sometimes defined by $C_M = \frac{1}{\rho}\left(\frac{\varepsilon_s-1}{\varepsilon_s+2}\right) = \frac{4\pi A}{3W}\alpha_o$, but (II:2) is the more common definition. Density ρ is most frequently quoted in amagat units, but often in moles/ℓ. Note that 1 mole/ℓ = 22.39 amagats. One amagat is defined as the number of molecules per unit volume in a perfect gas at N.T.P., viz: $2.689\text{x}10^{19}\ \text{cm}^{-3}$.

At optical frequencies (II:1) is to be replaced by the Lorentz-Lorenz formula:

$$\frac{n^2(\omega)-1}{n^2(\omega)+2} = \frac{4\pi}{3} N_o \alpha(\omega) \qquad \text{(II:3)}$$

where $n(\omega)$ is the refractive index at the frequency and $\alpha(\omega)$ is the polarizability of the isolated particle at that frequency. From (II:3) it then follows that at a given frequency, ω, the Lorentz-Lorenz function:

$$L(\omega) = \frac{W}{\rho}\left(\frac{n^2-1}{n^2+2}\right) = \left(\frac{4\pi A}{3}\right)\alpha(\omega) \qquad \text{(II:4)}$$

should also be a constant independent of density and temperature.

(a) Experimental Background

Experiments to test the constancy of C_M given by (II:2) for simple nonpolar gases such as Ar, Kr, He, Ne, N_2, H_2, CO_2 and CH_4 have been carried out since the early 1930's - see, for example: Michels and Michels [1]; Michels, Jaspers and Saunders [2]; Michels, Saunders and Schipper [3]; Michels and Kleerekoper [4]; Michels, Ten Seldam and Overdijk [5]; Johnston, Outermans and Cole [6]; Johnston and Cole [7]; Orcutt and Cole [8], [9]. Most of the American work referred to here was painstakingly accurate but carried out only at low or modest densities (0 ~ 200 amagats, say), but the Dutch work quoted used densities as high as 600 ~ 800 amagats.

The results show that for most nonpolar gases C_M is not quite a constant, but rises as density is increased to a weak, broad maximum for densities in the range 200 ~ 300 amagats, after which it decreases slowly as density is further increased. Generally, it is also observed that C_M shows a weak temperature dependence at all densities.

Experimental data for argon taken from Michels, Ten Seldam and Overdijk [5] are shown in Fig. 1:a at temperatures of 25°C and 100°C. Naturally, the experimental error is largest at the lower densities since here $\varepsilon - 1$ is very small. It may be noticed that over the whole range of density

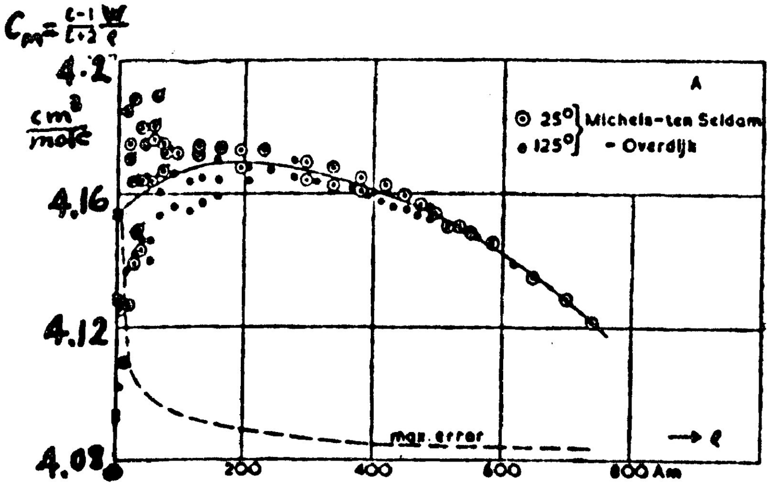

FIG. 1. Clausius-Mosotti function of argon (Ref. [5]).

the variation of C_M is less than 1.6% in argon. Fig. 2 shows experimental results for CO_2 taken from Michels and Kleerekoper [4], at temperatures of 50°C and 100°C. Here C_M varies by about 2.8% over the density range shown. The temperature dependence of C_M is also more pronounced than for argon. Again, of course, the measurement errors are largest at the lower densities.

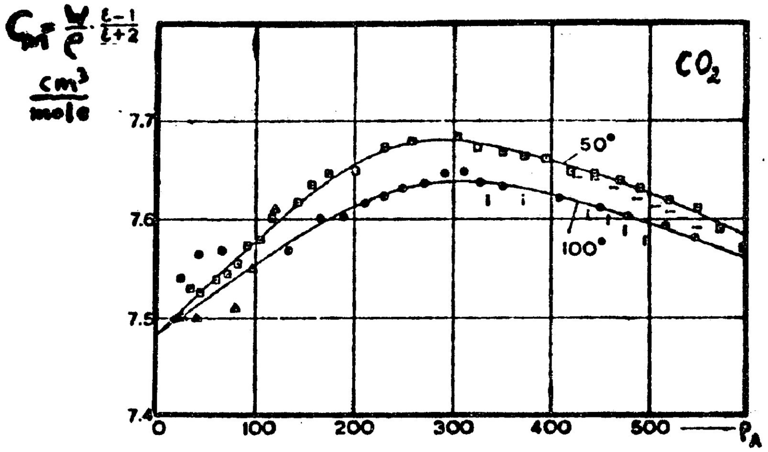

FIG. 2. Clausius-Mosotti function for carbon dioxide (Ref. [4]).

The results depicted for Ar and CO_2 are fairly typical of those obtained for simple nonpolar atomic and molecular gases, respectively, but it may be mentioned that for the light atomic gases, He and Ne, the recent measurements by Vidal and Lallemand [10] indicate that C_M does *not* exhibit a maximum in the density range of approximately 100 ~ 900 amagats. In fact, in this range C_M is observed to decrease almost linearly with increasing density and the maximum, if it exists, must occur at well below 100 amagats. For both these gases the overall change in C_M is very small - less than 1%. Similarly for molecular hydrogen, Michels, Sanders and Schipper [3] found that within experimental error *no* change at all could be observed in C_M in the density range 10-1000 amagats.

Measurements of C_M are usually carried out at audio or radio frequencies and no frequency dependence of C_M has been reported at these very long wavelengths. However, at optical frequencies where $L(\omega)$, given by (II:4), should be

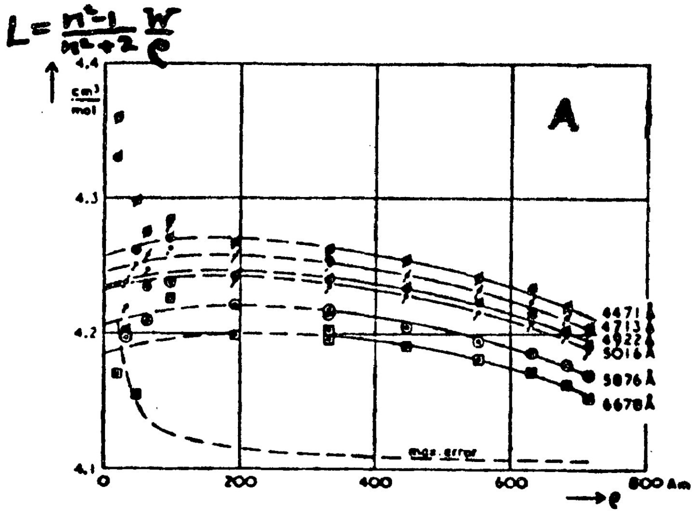

FIG. 3. Lorentz-Lorenz functions of argon at 25°C for various wavelengths (Ref. [11]).

independent of ρ and T, there also appears to be a paucity of experimental data. Fig. 3 shows the results for Ar given by Michels and Botzen [11] at various wavelengths in the range 4471°A-6678°A, all at 25°C. It may be observed that for a given wavelength the L vs. ρ curve has the same general shape as the C_M vs. ρ shown in Fig. 1.

Measurements of $L(\omega)$ vs. ρ for other gases, notably CO_2, N_2 and CH_4 were carried out by Michels and Hamers [12], Michels, Lebesque and de Groot [13], and Michels, Botzen and de Groot [14], with essentially the same general results as for Ar; viz. an increase in $L(\omega)$ to a maximum followed by a decrease in $L(\omega)$ as density is further increased.

(b) Theoretical Background

The fact that C_M and $L(\omega)$ are nearly constant with changes in ρ and T indicates that use of the Lorentz local field to calculate the moment induced into a given nonpolar molecule is indeed a very good approximation. It will be recalled from elementary dielectric theory, Fröhlich [15], that the Lorentz field is calculated as that existing inside a spherical specimen of radius so large that it has the macroscopic dielectric properties of the medium. This field arises from sources inside and outside the sphere and for a cubic lattice or a homogeneous, isotropic medium the former vanishes. However, the latter is given by the combined contributions of the macroscopic field, $\underset{\sim}{E}$ less the self-field, $\underset{\sim}{E}_s = -\frac{4\pi}{3}\underset{\sim}{P}$ of the homogeneously polarized sphere. The Lorentz local field is thus:

$$\underset{\sim}{F} = \underset{\sim}{E} + \frac{4\pi}{3}\underset{\sim}{P} \qquad \text{(II:5)}$$

independent of the radius of the spherical specimen.

Equation (II:5) leads at once to the macroscopic, Clausius-Mossotti formula (II:1) but as pointed out by Fröhlich, [15], (App. 3), (II:1) may also be regarded as a molecular formula provided short-range (non-dipolar) forces are neglected and the molecular volume is chosen equal to the volume available per molecule, viz:

$$\frac{4\pi}{3}a^3 = \frac{1}{N_o} \qquad \text{(II:6)}$$

In this case (II:1) becomes the Clausius-Mossotti formula for a single molecule, viz:

$$\frac{\varepsilon_s-1}{\varepsilon_s+2} = \frac{\alpha_o}{a^3} \qquad \text{(II:7)}$$

Here a is the "dielectric" molecular radius. When (II:7) holds it follows that α_o/a^3 is proportional to the density which may be varied by changing the external pressure.

Kirkwood [16] was the first to realize that Lorentz's calculation of the local field, while probably valid in a solid cubic lattice, is suspect for a gas or liquid since it takes no account of the comparatively large density fluctuations that occur in fluids. This means in a fluid that considering the medium surrounding the sphere (in Lorentz's theory) to be a homogeneous, isotropic continuum may be too strong an approximation and an approach based on a medium with particulate structure would be more satisfactory.

Kirkwood assumed only dipolar interparticle forces need be considered and that the particle polarizability, α_o was independent of density. Since his model was based entirely on a particle picture there was no need to introduce the ingeneous device of the "Lorentz sphere" at the outset. The moment induced into the i^{th} nonpolar molecule is then:

$$\underset{\sim}{p}_i = \alpha_o \underset{\sim}{F}_i = \alpha_o(\underset{\sim}{D} - \sum_{j\neq i} \underset{\sim}{T}_{ij} \cdot \underset{\sim}{p}_j) \qquad \text{(II:8)}$$

where $\underset{\sim}{F}_i$ is the local field and $T_{ij} = r_{ij}^{-3}(I - \underset{\sim}{r}_{ij}\underset{\sim}{r}_{ij}/r_{ij}^2)$ is the dipole-dipole interaction tensor. The problem remaining is to find the average value $\bar{\underset{\sim}{p}}_i$ of $\underset{\sim}{p}_i$ using standard techniques of statistical physics. In this connection it may be noted, as shown by Kirkwood, that the calculation of $\bar{T}_{ij}$ introduces in a natural way a small sphere of indefinite radius surrounding the i^{th} molecule. This is equivalent to the Lorentz sphere introduced in the earlier theory.

At very low densities, where correlation between $\bar{p}_j$ and $\bar{T}_{ij}$ is negligible, the results show that the Clausius-Mossotti formula is recovered, but as the density increases, and correlation becomes more important, C_M rises to a very weak maximum usually at higher densities than observed experimentally. C_M then falls more slowly with increasing density than found experimentally. Kirkwood's [16] results for argon compared to the experimental results of Michels et al. [5] are shown in Fig. 4.

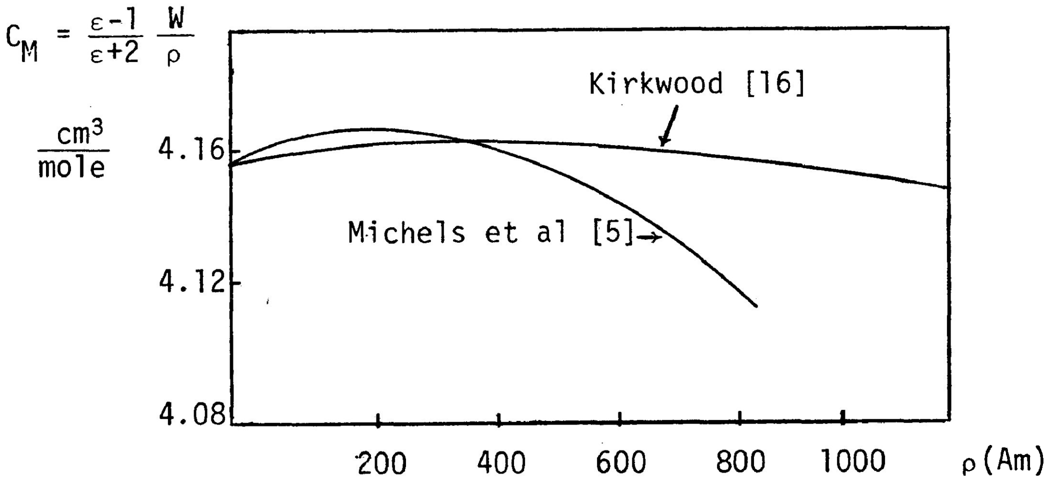

FIG. 4. Kirkwood's theory [16] for argon compared to experimental results of Michels et al. [5].

The fact that C_M calculated by Kirkwood rises more slowly with increasing density than indicated by experiment at low densities, and falls less rapidly at high density prompted other workers to examine the fluctuation theory more carefully. Thus Mandel and Mazur [17] took steps to remove the shape dependence of the dielectric sample in Kirkwood's theory. Earlier, de Boer, Vander Maesen and Ten Seldam [18], had introduced the effect of short-range repulsive forces between particles by means of the Lennard-Jones and the Hertzfeld potentials. As expected their results show a more rapid decrease of C_M vs. ρ at high densities, but too slow an increase of C_M with increasing ρ at low densities.

Jansen and Mazur [19], [20] were the first to treat the particulate theory using quantum mechanics. They limited themselves to spherical molecules undergoing dipolar interaction only and found for H and He that the initial increase of C_M with increasing density was of the same order of magnitude as predicted by Kirkwood's theory. It should be stressed that unlike Kirkwood's theory, Jansen and Mazur took account of the fact that the polarizability of the particle was density dependent, but as in Kirkwood's theory short-range repulsive forces were ignored. Later, Jansen and Salem [21] extended the above theory to include the first few low-order multipole moments for the rare gases and simple diatomic molcules, but finally Jansen [22] concluded that within the range of experimental error in the measurements this theory does *not* account for the observed results.

A somewhat different approach to the problem was taken by Michels, de Boer and Bijk [23]; de Groot and Ten Seldam [24], [25]; and Ten Seldam and de Groot [26], [27]. These authors concerned themselves with the change in energies and wave functions of atoms when the electrons are localized to a finite region of space surrounding the atom. This step essentially confines the electrons to a suitably shaped box at whose sides the potential becomes infinite and at which the wave function must vanish. Thus

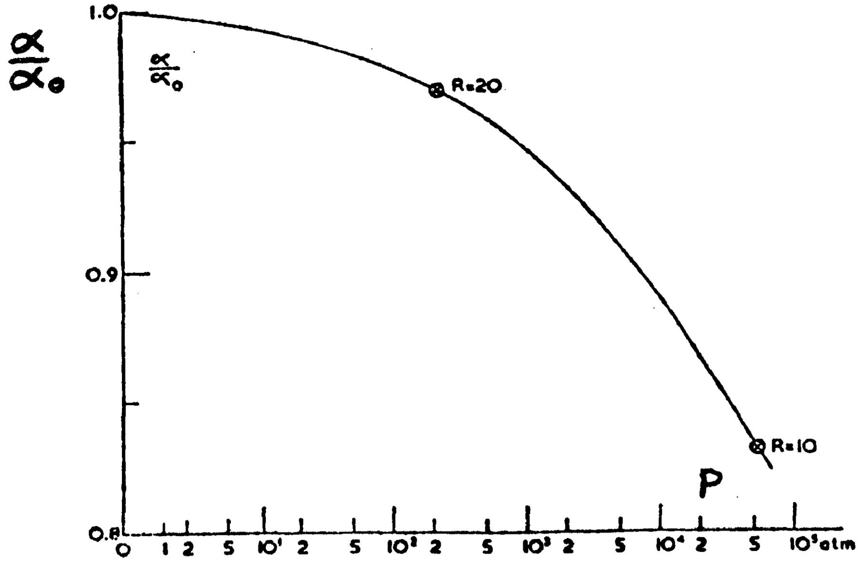

FIG. 5. Polarizability of helium as a function of pressure: Ten Seldam and de Groot (Ref. [27]).

Ten Seldam and de Groot [27] considered an He atom confined to a sphere of radius r_o and used the change in energies and wave functions to find the change in polarizability of the confined He atom. As expected, α/α_o decreases smoothly with increasing density without sign of a maximum. The result is shown in Fig. 5.

It may be noted that, in a sense, this model represents a return to the Lorentz "continuum" model except that dipolar interaction between the caged atomic electrons and all others in the medium surrounding the sphere has been ignored. However, the repulsive forces, which tend to confine the electron to the sphere surrounding the nucleus, have been taken into account. Of course, density fluctuations in the dipolar interaction between the molecule and the surrounding medium are not considered in the Ten Seldam and de Groot model.

At this point it may be mentioned that in the area of a continuum theory for C_M, Böttcher [28], some years ago, proposed interpreting the Onsager formula for nonpolar materials in a certain way to try and explain the observed deviations from the Clausius-Mossotti formula.

It will be recalled for a nonpolar medium that Onsager's formula gives the permittivity from:

$$\frac{(\varepsilon_s-1)(2\varepsilon_s+1)}{12\pi\varepsilon_s} = \frac{N_o\alpha_o}{1-\alpha_o g} \qquad \text{(II:9)}$$

where N_o is the number density of particles of polarizability α_o and

$$g = \frac{2(\varepsilon_s-1)}{2\varepsilon_s+1} \cdot \frac{1}{a^3} \qquad \text{(II:10)}$$

is the reaction field factor for molecules of radius a. It is usual in the Onsager theory to reduce (II:9) to the Clausius-Mossotti formula (II:1) by insisting that the particle volume equals the volume available to it according to (II:6), but Böttcher declined taking this step and instead treated $u = \alpha_o/a^3$ as a *constant* independent of density for each particular substance. In this way he finds a modified C_M function:

$$C_M = C_M^{(o)} f(\varepsilon_s) \qquad \text{(II:11:a)}$$

where $C_M^{(o)} = 4\pi A\alpha_o/3$ is the C_M function at zero density and

$$f(\varepsilon_s) = \frac{9\varepsilon_s}{(\varepsilon_s+2)\left[(2\varepsilon_s+1)-2(\varepsilon_s-1)u\right]} \; . \qquad \text{(II:11:b)}$$

For $\varepsilon_s = 1$ it is readily seen that $C_M = C_M^{(o)}$, but for other values of the permittivity $f(\varepsilon_s)$ will at first increase to a maximum and then decrease as ε_s (and thus the density) is further increased. In this way, with appropriate choices for u, Böttcher obtains C_M vs. ρ curves which fit the experimental data remarkably well for gases such as CO_2.

However, there is a fundamental difficulty in Böttcher's argument that α_o/a^3 is a constant independent of density for from (II:9) and (II:10) we may readily compute the quantity $X = \frac{4\pi}{3} N_o a^3$ to be:

$$X = \frac{\varepsilon_s - 1}{\varepsilon_s + 2} \left[uf(\varepsilon_s) \right]^{-1} \quad . \qquad \text{(II:12)}$$

In Onsager's theory X = 1 at all densities, but for Böttcher's idea we may always plot X vs. ρ using experimental results of ε_s vs. ρ. For CO_2, for example, it may be shown that X decreases very slowly and almost linearly with increasing density. Extrapolating this result to $\rho = 0$ leads to a non-vanishing value $X = X_o$ at zero density ($X_o = 1.55$ for CO_2), and hence when $N_o = 0$, $a^3 \longrightarrow \infty$. It follows that at zero density α_o must also be infinite, a result in conflict with the observations that the polarizability of an isolated atom or molecule is a *finite* quantity.

(c) The Present Theory

It is apparent from the above review that there have been two main approaches to a theory of the Clausius-Mossotti function, $C_M(\rho,T)$ in dense gases. The first of these is the "density-fluctuation" theory initiated by Kirkwood (loc. cit.) and the second the "continuum" theory initiated by de Groot and Ten Seldam (loc. cit.). To date there appears to be no theory which unifies both approaches simultaneously. However, the continuum theory has the advantage of predicting results at high densities which are beyond the accessible range of calculation of fluctuation theories - because of the need to take account of higher and higher orders of multipole interactions as the density rises. For this reason the present work favours the continuum approach.

It is clear that a major improvement to the de Groot and Ten Seldam theory would be to include the effect of long-range dipolar interaction between the caged nonpolar particle and the surrounding medium. The effect of this interaction would be to attract the electron away from the core and thus lower the effective oscillator frequency of the caged electron and hence increase the polarizability. This would be the predominant effect at low densities. On the other hand, at high densities, where each electronic oscillator finds itself increasingly restricted by a δ-like potential at the surface of the cage as density is raised, the energy would tend to increase and result in a reduction of polarizability. Qualitatively, therefore, as density is increased the polarizability would at first increase, pass through a maximum and then decrease at higher densities in agreement with experimental observation.

For long wavelength, dipole oscillations, where the fields are essentially electrostatic, it is not difficult to formulate the above idea quantitatively since the general technique for finding the potentials associated with an extended, eccentric dipole in a spherical cavity were given some time ago by Frood and Dekker [29]. For example, in the present problem a straightforward calculation (Frood [30]) of the reaction field of an extended, electronic dipole in a sphere of radius "a" with a fixed, centralized core charge, +e leads to the self-energy of the dipole in its own reaction field, viz:

$$V_{\underline{self}} = -\frac{e^2}{a}\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)\left(\frac{r}{a}\right)^2 \sum_{n=0}^{\infty} B_n(\varepsilon)\left(\frac{r}{a}\right)^{2n} \qquad (II:13)$$

where:

$$B_n(\varepsilon) = \frac{(n+2)(2\varepsilon+1)}{2\left[(n+2)\varepsilon+(n+1)\right]}$$

and where $r \leq a$ is the position of the electron. The total potential in which the electron moves is then the sum of (II:13) and the atomic potential ($-e^2/r$ for hydrogen) which must then be inserted in the Schrödinger equation and the latter solved under the condition $\psi(r = a) = 0$.

Leaving aside for the moment the formidable mathematical difficulties consequent upon this step, it will be noticed that (II:13) depends explicitly on the quantity, ε which we desire to calculate. Thus, as used in the calculation of, say, a polarizability, (II:13) requires that the permittivity be calculated self-consistently with the result! A further difficulty inherent in (II:13) is that it diverges at $r = a$. For these reasons we do not pursue here a calculation for 3-dimensional atoms, but instead go directly to the more tractable case of a 1-dimensional model. As will be seen in Sec. III the self-energy of the 1-dimensional dipole in its own local field is then not explictly dependent on ε except through the polarization, $\underset{\sim}{P}$, which is the quantity we wish to calculate. In addition, there is no divergence in this 1-dimensional self-energy.

In Sec. III:a we review the well known calculation of the Clausius-Mossotti formula from the Onsager point of view, and in Sec. III:b:(i) we introduce the 1-dimensional model and the corresponding 1-dimensional Clausius-Mossotti formula for an unrestricted oscillator experiencing dipolar interaction with its neighbors. In Sec. III:(b):(ii) we then restrict this oscillator by assuming short-range forces introduce a δ-function potential which confines the oscillator to a finite slab of thickness $2x_o$. We treat this problem quantum mechanically and require the wave function to vanish at $x = \pm x_o$. Here the computer is a natural tool since the range of the independent variable is finite for a restricted oscillator, and it is easy to discretize the interval $-x_o \leq x \leq x_o$.

In Sec. IV we compute the energies and wave functions of the restricted S.H.O. *without* dipolar interaction. The wave functions and energies so calculated are then used in perturbation theory to give the ground state polarizability as a function of density. As expected, the polarizability decreases smoothly as density increases in this model. In Sec. V we consider the same problem as in Sec. IV, but *with* dipolar interaction present and again compute the ground state polarizability. As expected, for this more realistic model there is a definite maximum in α vs. ρ which occurs in the density range 200 $\sim$ 300 am for Ar, Kr, CO_2 and N_2.

In Sec. VI we calculate the polarizabilities of the excited states of a restricted 1-dimensional S.H.O. experiencing dipolar interaction with a view to investigating the temperature dependence of the C_M function. As may be expected, our model shows this effect to be negligible in view of the rather large energy gaps between the different states. However, here a surprising result occurs, namely, that at sufficiently high densities the polarizability of any excited state can become *negative*. This suggests that these states are those of free electrons rather than bound oscillators and provides, qualitatively, a suggestion for a completely different model in which a particle oscillator should, at the outset, be characterized as having a finite, density-dependent activation energy. Furthermore its interaction with other oscillators in the surrounded medium should occur through *screened* dipolar forces as suggested some time ago by Frood [31] for a closely related model. Discussion of this idea is considered in Sec. VIII, but in Sec. VII we compare our results for the dielectric constants of Ar, Kr, CO_2 and N_2 with experimental values and as will be seen there is fair agreement for comparison of experimental and theoretical ε vs. ρ, but only qualitative agreement for the same comparison of C_M functions.

The hard copy of the computer programmes which form Appendices A, B, C and D are printed as a separate document accompanying this thesis.

III. THE MODEL

(a) 3-Dimensional, Unrestricted Simple Harmonic Oscillator with Dipolar Interaction.

Consider a point dipole $\vec{m}$ at the centre of a sphere of radius a and dielectric constant ε_i. This sphere is surrounded by a medium of dielectric constant ε. The whole is in an electric field $\vec{E}$ which is uniform at infinity and parallel to the dipole $\vec{m}$. The potential V_o outside the sphere satisfies Laplace's equation $\nabla^2 V_o = 0$, since there are no free charges except those at great distance required to maintain the macroscopic electric field $\vec{E}$. The potential V_i inside the sphere consists of the potential of the source dipole $\vec{m}$ and the potential Φ_i which satisfies Laplace's equation $\nabla^2 \Phi_i = 0$.

Let us set up a spherical coordinate system so that the Z-axis is parallel to $\underset{\sim}{E}$ (and $\underset{\sim}{m}$) with origin at the centre of the sphere (Fig. 6).

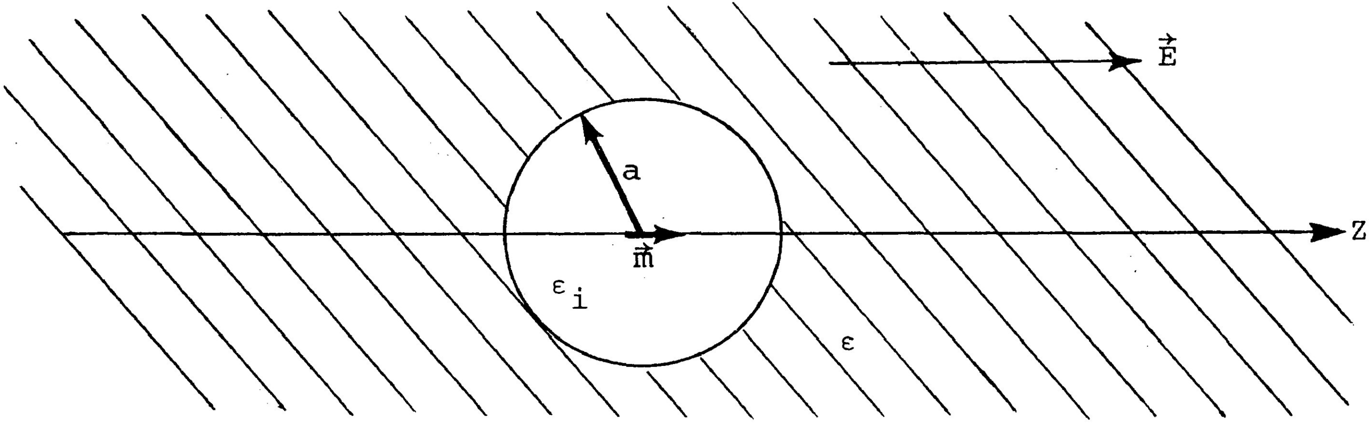

FIG. 6. Induced point dipole in spherical cavity.

A general solution of Laplace's equation in spherical coordinates r, θ and ϕ is:

$$V = \sum_{n=0}^{\infty} \sum_{n=0}^{\infty} \left[A_{mn} r^n + \frac{B_{mn}}{r^{n+1}} \right] P_n^m(\cos\theta) e^{im\phi} \qquad \text{(III:1)}$$

Since the system is spherically symmetrical, the potential both inside and outside are independent of the azimuthal angle. Thus the potential V_o outside the sphere is equal to:

$$V_o(r,\theta) = \sum_{n=0}^{\infty} \left(A_n r^n + \frac{B_n}{r^{n+1}} \right) P_n(\cos\theta) \qquad \text{(III:2)}$$

Because the potential must not have a singularity at the centre of the sphere (r=0), we require:

$$\Phi_i = \sum_{n=0}^{\infty} C_n r^n P_n(\cos\theta) \qquad \text{(III:3)}$$

and hence the potential V_i inside is:

$$V_i(r,\theta) = \Phi_i + V_{dipole} = \sum_{n=0}^{\infty} C_n r^n P_n(\cos\theta) + \frac{m}{\varepsilon_i r^2} \cos\theta \qquad \text{(III:4)}$$

The boundary conditions are:

At $Z \longrightarrow \infty$ the potential outside must reduce to:

$$V_o(r,\theta) = -EZ = -Er\cos\theta \qquad \text{(III:5)}$$

and

$$V_i(a,\theta) = V_o(a,\theta) \qquad \text{(III:6)}$$

since the potential is continuous across the boundary. Also:

$$\varepsilon_i \left(\frac{\partial V_i}{\partial r}\right)_{r=a} = \varepsilon \left(\frac{\partial V_o}{\partial r}\right)_{r=a} \qquad \text{(III:7)}$$

because the normal component of $\vec{D}$ must be continuous at the boundary.

Since the field at $Z \longrightarrow \infty$ is $\frac{\partial V_o}{\partial r} = -E$ then all the coefficients A_n are zero except A_1, which has the value $A_1 = -E$, and the potential V_o outside the sphere is therefore:

$$V_o(r,\theta) = -Er\cos\theta + \sum_{n=0}^{\infty} \frac{B_n}{r^{n+1}} P_n(\cos\theta) \qquad \text{(III:8)}$$

Applying the second and third boundary conditions to (III:4) and (III:8), and recalling the orthogonality properties of

Legendre's polynomials we easily obtain:

$$C_n a^n + \frac{m}{\varepsilon_i a^2} \delta_{n,1} = -Ea\delta_{n,1} + \frac{B_n}{a^{n+1}} \qquad \text{(III:9)}$$

and:

$$n\varepsilon_i C_n a^{n-1} - \frac{2m}{a^3} \delta_{n,1} = -\varepsilon E\delta_{n,1} - \frac{\varepsilon(n+1)B_n}{a^{n+2}} \qquad \text{(III:10)}$$

For n ≠ 1, these two equations become:

$$C_n a^n = \frac{B_n}{a^{n+1}} \qquad \text{(III:11)}$$

and

$$n\varepsilon_i C_n a^{n-1} = - \frac{\varepsilon(n+1)B_n}{a^{n+2}} \qquad \text{(III:12)}$$

From these last two equations it follows that $B_n = 0$ and $C_n = 0$ for all values of n except n = 1. When n = 1, we have:

$$C_1 + \frac{m}{\varepsilon_i a^3} = -E + \frac{B_1}{a^3} \qquad \text{(III:13)}$$

and:

$$\varepsilon_i C_1 - \frac{2m}{a^3} = -\varepsilon E - \frac{2\varepsilon B_1}{a^3} \qquad \text{(III:14)}$$

and solving (III:13) and (III:14) for B_1 and C_1, there results:

$$B_1 = \frac{(\varepsilon_i-\varepsilon)a^3}{(2\varepsilon+\varepsilon_i)} E + \frac{3m}{(2\varepsilon+\varepsilon_i)} \qquad \text{(III:15)}$$

$$C_1 = -\frac{3\varepsilon}{(2\varepsilon+\varepsilon_i)} E + \frac{2(\varepsilon_i-\varepsilon)}{\varepsilon_i(2\varepsilon+\varepsilon_i)} \frac{m}{a^3} \qquad \text{(III:16)}$$

(i) Cavity Field

Suppose $\vec{m} = 0$, then we have a dielectric ε_i imbedded in a dielectric ε_o. For this case:

$$B_1 = \frac{(\varepsilon_i-\varepsilon)a^3}{(2\varepsilon+\varepsilon_i)} E \qquad \text{(III:17)}$$

$$C_1 = \frac{-3\varepsilon}{2\varepsilon+\varepsilon_i} E \qquad \text{(III:18)}$$

The field inside the sphere is thus homogeneous and in the same direction as E, and is given by:

$$-\frac{\partial V_i}{\partial Z} = \frac{3\varepsilon}{2\varepsilon+\varepsilon_i} E \qquad \text{(III:19)}$$

If in particular $\varepsilon_i = 1$, we have what is referred to as the "cavity field"

$$\vec{E}_c = \frac{3\varepsilon}{2\varepsilon+1} \vec{E} \qquad \text{(III:20)}$$

(ii) Reaction Field

Consider now $\vec{E} = 0$ so that we have a point dipole at the centre of a sphere of dielectric constant ε_i embedded in the medium of dielectric constant ε. For this case the field inside the sphere is given by:

$$-\frac{\partial V_i}{\partial Z} = \frac{2(\varepsilon-\varepsilon_i)}{\varepsilon_i(2\varepsilon+\varepsilon_i)}\frac{m}{a^3} - \frac{m}{r^3}(1-3\cos^2\theta) \qquad \text{(III:21)}$$

The second term of (III:21) is the Z-field of the point dipole $\vec{m}$. The first term of (III:21) is:

$$\vec{R} = \frac{2(\varepsilon-\varepsilon_i)}{\varepsilon_i(2\varepsilon+\varepsilon_i)}\frac{\vec{m}}{a^3} \qquad \text{(III:22)}$$

This is clearly the field inside the sphere due to the polarized charges on both the inside and outside surfaces of the sphere. These polarized charges arise, of course, from the "source" dipole $\vec{m}$. For $\varepsilon_i = 1$, we have what is called the "reaction field":

$$\vec{R} = \frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{\vec{m}}{a^3} \qquad \text{(III:23)}$$

This field has the direction of $\vec{m}$ and is due to the polarized charges on the outside surface of the sphere which are considered fixed before the dipole and the dielectric sphere are removed. Note also for a central, point dipole that the reaction field is homogeneous. However, as discussed in Sec. III:(c), for an extended dipole or for a point dipole which is not located at the centre of the cavity, the reaction field is not homogeneous.

(iii) Local Field (Onsager Theory)

Suppose now we fix the state of polarization in the medium outside the sphere and remove the sphere and its polarization from the dielectric, what is the total field inside the cavity? Clearly the field is given by Onsager's expression F = (Cavity field) + (Reaction field of point dipole), that is:

$$\vec{F} = \vec{E}_c + \vec{R}$$

$$= \frac{3\varepsilon}{3\varepsilon+1}\vec{E} + \frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{\vec{m}}{a^3} \qquad \text{(III:24)}$$

But for a homogeneously polarized sphere:

$$\vec{m} = \frac{4\pi}{3}a^3\vec{P} \qquad \text{(III:25)}$$

where:

$$\vec{P} = \frac{\varepsilon-1}{4\pi}\vec{E} \qquad \text{(III:26)}$$

is the polarization of the medium. Substituting (III:26) into

(III:25) we get:

$$\frac{\vec{m}}{a^3} = \frac{\varepsilon-1}{3}\ \vec{E} \tag{III:27}$$

and employing (III:27) in (III:24) there results:

$$\vec{F} = \vec{E} + \frac{4\pi}{3}\vec{P} = \frac{\varepsilon+2}{3}\ \vec{E} \tag{III:28}$$

Eq. (III:28) is the well known Lorentz local field given earlier in (II:5). This field is independent of "a" the radius of the sphere.

The dipole moment can also be written as:

$$\vec{m} = \alpha_o\vec{F} \tag{III:29}$$

where α_o is the polarizability of the isolated molecule and $\vec{F}$ is the local field.

Since the total moment per unit volume is:

$$\underset{\sim}{P} = N_o\underset{\sim}{m} = N_o\alpha \left(\frac{\varepsilon+2}{3}\right) \underset{\sim}{E} \tag{III:30}$$

we find using (III:30) in (III:26) that:

$$\frac{\varepsilon-1}{\varepsilon+2} = 4\pi N_o\alpha_o \tag{III:31}$$

and (III:31) is just the Clausius-Mossotti formula for an assembly of nonpolar, spherical molecules as shown in Sec. I.

(b) 1-Dimensional, Unrestricted and Restricted Simple Harmonic Oscillators with Dipolar Interaction.

(i) Unrestricted Oscillator

Consider a dipole with the positive charge +q at the origin and the negative charge -q free to oscillate along the x-axis. The dipole is confined to a plane slab of thickness $2x_o$ of dielectric constant unity which is sandwiched between two, plane semi-infinite media of permittivity ε. These represent the "surrounding medium." The whole is in an electric field, E, which is uniform at infinity and parallel to the dipole (Fig. 7).

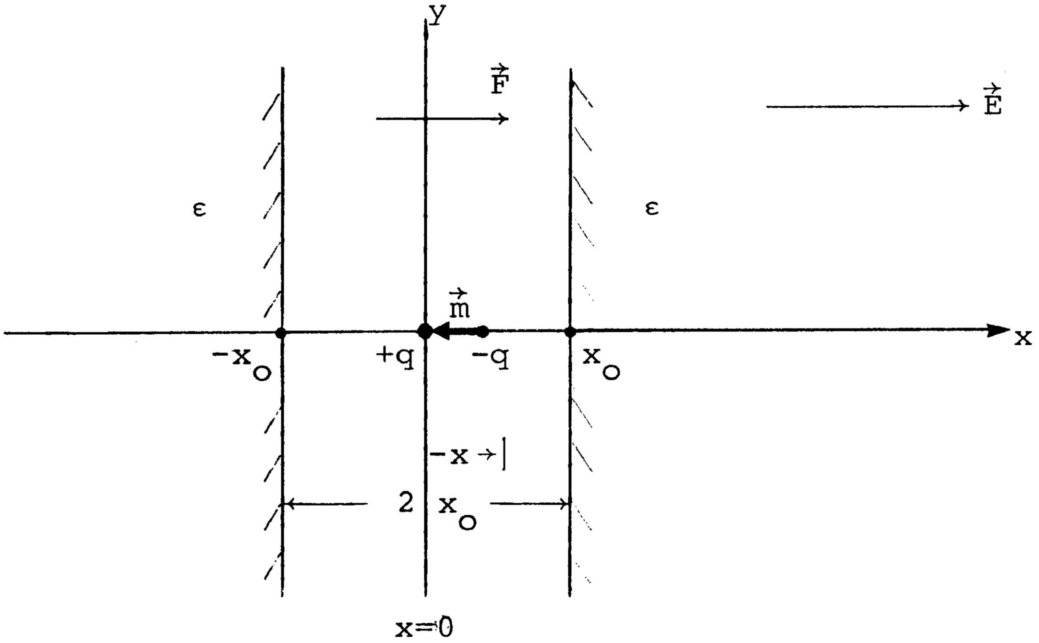

FIG. 7. Induced line dipolar in slab cavity.

To obtain the local field in this case by the Onsager method used in Sec. III:(a) is very difficult and tedious. The reaction field can be obtained using the method of images and results in a non-summable series of terms. The cavity field is equally difficult to compute, but bearing in mind that it is only the local field which is of interest, we may proceed in a straightforward manner as follows:

Because of the continuity of the normal displacement at the boundary, the local field, $\underset{\sim}{F}$ inside the cavity must be:

$$\vec{F} = \varepsilon\vec{E} = \vec{E} + 4\pi\vec{P} \qquad \text{(III:32)}$$

where $\vec{E}$ is the macroscopic field and $\vec{P}$ is the moment per unit volume which is also equal to:

$$P = -qN_o x \qquad \text{(III:33)}$$

Here N_o is the number density of molecules in the medium and x is the displacement of the charge -q. It should be noted that the local field (III:32) is homogeneous and independent of the length of the dipole. Making use of (III:32) and (III:33), the energy required to polarize the dipole is clearly:

$$W = q\int_{o}^{x} F dx$$

$$= -qEx + 4\pi N_o q^2\left(\frac{x^2}{2}\right) \qquad \text{(III:34)}$$

$$= -qEx + \frac{1}{2}m_o\omega_p^2 x^2 \qquad \text{(III:35)}$$

where:

$$\omega_p = \left(\frac{4\pi N_o q^2}{m_o}\right)^{\frac{1}{2}} \qquad \text{(III:36)}$$

is the plasma frequency of the bound electrons in the medium. Thus, taking account of the back-reaction of the medium, the total potential energy of the system is:

$$V = \frac{1}{2}m_o\omega_o^2 x^2 - \frac{1}{2}m_o\omega_p^2 x^2 + qEx \qquad \text{(III:37)}$$

where ω_o is the frequency of the isolated oscillator. The Lagrangian of the system is therefore:

$$L = T-V = \frac{1}{2}m_o\dot{x}^2 - \frac{1}{2}m_o\omega_o^2 x^2 + \frac{1}{2}m_o\omega_p^2 x^2 - qEx$$

$$= \frac{1}{2}m_o\dot{x}^2 - \frac{1}{2}m_o\omega_{eff}^2 x^2 - qEx \qquad \text{(III:38)}$$

where $\omega_{eff} = (\omega_o^2-\omega_p^2)^{\frac{1}{2}}$ is the density-dependent, effective frequency of the oscillator in interaction with its surroundings. The first two terms of (III:38) represent the Lagrangian of a dipolar simple harmonic oscillator, and the last term in (III:38) is the negative of the interaction energy between the macroscopic field, $\vec{E}$ and this dipole of moment $m = -qx$.

From classical mechanics the equation of motion of this oscillator is found from:

$$\frac{\partial}{\partial t}\left(\frac{\partial L}{\partial \dot{x}}\right) - \frac{\partial L}{\partial x} = 0 \qquad \text{(III:39)}$$

leading to:

$$\ddot{x} + \omega_{eff}^2 x = -\frac{q}{m_o} E \qquad \text{(III:40)}$$

For an oscilllating field of the form:

$$\vec{E}(t) = \vec{E}_o e^{i\omega t} \qquad \text{(III:41)}$$

an immediate particular solution of (III:40) is:

$$\vec{x}(t) = -\frac{q}{m_o} \frac{\vec{E}_o e^{i\omega t}}{\omega_{eff}^2 - \omega^2} \qquad \text{(III:42)}$$

Next using (III:42) in (III:33) the polarization becomes:

$$\vec{P}(t) = \frac{q^2 n_o}{m_o} \frac{\vec{E}_o e^{i\omega t}}{\omega_{eff}^2 - \omega^2} \qquad \text{(III:43)}$$

leading at once to:

$$\frac{\varepsilon - 1}{4\pi} \vec{E} = \frac{q^2 N_o}{m_o} \frac{\vec{E}_o e^{i\omega t}}{\omega_{eff}^2 - \omega^2} \qquad \text{(III:44)}$$

and using (III:41) in (III:44) the frequency dependent dielectric constant is thus:

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{(\omega_o^2 - \omega_p^2) - \omega^2} \qquad \text{(III:45)}$$

Hence:

$$\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega)} = \frac{\omega_p^2}{\omega_o^2 - \omega^2} \qquad \text{(III:46)}$$

For static fields ($\omega=0$), (III:46) becomes:

$$\frac{\varepsilon_s - 1}{3\varepsilon_s} = \frac{\omega_p^2}{3\omega_o^2} = \frac{4\pi N_o}{3} \alpha_o \qquad \text{(III:47)}$$

where $\alpha_o = \frac{e^2}{m\omega_o^2}$ is the polarizability of the isolated simple harmonic oscillator.

Eq. (III:47) is just the Clausius-Mossotti formula for a 1-dimensional unrestricted simple harmonic oscillator interacting with dipolar forces with its neighbours. The factor 1/3 is introduced on both sides of (III:47) so that the right hand side corresponds with that for the 3-dimensional Clausius-Mossotti formula given by (I:1) and (III:31).

(ii) Restricted Oscillator

Consider the system which is described in (III:b:i), but now the dipole is restricted by infinite potential barriers at $x = \pm x_o$. In other words, the dipole oscillates only in the region between $-x_o$ and x_o. This potential barrier represents the effect of the repulsive forces between the charge -q and the "whole surrounding medium." The latter is considered to be a homogeneous, isotropic medium with dielectric constant ε (Fig. 7). Since the normal component of $\vec{D}$ must be continuous at the boundary, the local field, $\underset{\sim}{F}$, inside the cavity must still be given by (III:32), viz:

$$\vec{F} = \varepsilon\vec{E} = \vec{E} + 4\pi\vec{P} \tag{III:48}$$

where $\underset{\sim}{E}$ is the macroscopic field and $\underset{\sim}{P}$ is the moment per unit volume. $\underset{\sim}{F}$ is also homogeneous and independent of the length of the dipole, provided this length is less than x_o. Comparing (III:32) with (III:48), we concluded that the local field,

$\underset{\sim}{F}$, for both unrestricted and restricted oscillators are the same. Thus, the energy required to polarize the dipole is given by (III:35). The classical Hamiltonian of the system is therefore:

$$H = \frac{p^2}{2m_o} + \frac{1}{2} m_o \omega^2_{eff} x^2 + qEx \qquad \text{(III:49)}$$

where $p = m_o \dot{x}$ is the momentum of the charge $-q$ and $\omega^2_{eff} = (\omega_o^2 - \omega_p^2)$ is the density-dependent, effective frequency of the oscillator in interaction with its surroundings. The first two terms of (III:49) represent the Hamiltonian of a simple harmonic (dipole) oscillator, and the last term is the interaction energy between the dipole of moment $m = -qx$ and the macroscopic field, $\vec{E}$. Since the charge $-q$ is restricted by infinite potential barriers, its wave function must vanish for $|x| \geq x_o$. When we consider the quantum nature of this system, the Hamiltonian of interest is:

$$H = -\frac{\hbar^2}{2m_o} \frac{d^2}{dx^2} + \frac{1}{2} m_o \omega^2_{eff} x^2 + qEx \qquad \text{(III:50)}$$

where m_o is the mass of the charge $-q$ and $\hbar$ is Planck's constant. The Schrödinger equation of the system is thus:

$$-\frac{\hbar^2}{2m_o} \frac{d^2\Psi}{dx^2} + \frac{1}{2} m_o \omega^2_{eff} x^2 \Psi + qEx\Psi = W\Psi \qquad \text{(III:51)}$$

and the wave function $\Psi(x)$ is required to vanish at $x = \pm x_o$, i.e.

$$\Psi(-x_o) = \Psi(x_o) = 0 \tag{III:52}$$

It is usual to solve (III:51) by an exact method, that is, by introducing a new coordinate

$$x' = x + \frac{qE}{m_o\omega^2_{eff}} \tag{III:53}$$

then the wave equation becomes

$$-\frac{\hbar^2}{2m_o}\frac{d^2\Psi(x')}{dx'^2} + \frac{1}{2}m_o\omega^2_{eff}x'^2\Psi(x') = \left(W + \frac{2q^2E^2}{m_o\omega^2_{eff}}\right)\Psi(x') \tag{III:54}$$

but here the boundary conditions for the wave functions are:

$$\Psi\left(-x_o + \frac{qE}{m_o\omega^2_{eff}}\right) = \Psi\left(x_o + \frac{qE}{m_o\omega^2_{eff}}\right) = 0 \tag{III:55}$$

Since the wave functions depend upon a new coordinate, x', which is itself dependent on the macroscopic field, E, the new energy $W' = W + \frac{2q^2E^2}{m_o\omega^2_{eff}}$ and the wave function $\Psi(x')$ are dependent on E in a more complicated way than for the unrestricted oscillator. We could in principle solve the

Schrödinger equation numerically for a range of fields, E, and extrapolate our results to zero field, but this is clearly a complicated procedure and we elect instead to use a perturbation method described below:

Let us assume that the macroscopic field is so small that qEx can be treated as a perturbation, then the Schrödinger equation can be written:

$$(H_o + H')\Psi = W\Psi \tag{III:56}$$

where

$$H = -\frac{\hbar^2}{2m_o}\frac{d^2}{dx^2} + \frac{1}{2}m_o\omega_{eff}^2 x^2 \tag{III:57}$$

is the unperturbed Hamiltonian and

$$H' = qEx \tag{III:58}$$

is the perturbation potential energy.

The solution of the Schrödinger equation in the absence of both dipolar interaction ($\omega_p = 0$) and a macroscopic field, E, but with a wave function which vanishes at $|x| = x_o$ will be discussed in Sec. IV. Later, in Sec. V, the solution of the Schrödinger equation in the absence of a macroscopic field, E, but with dipolar interaction present and again with a wave function which vanishes at $|x| = x_o$ will be discussed.

IV. COMPUTED ENERGIES, WAVE FUNCTIONS AND STATIC POLARIZABILITY OF THE RESTRICTED SIMPLE HARMONIC OSCILLATOR WITHOUT DIPOLAR INTERACTION

Consider a simple harmonic oscillator which is restricted at $x = \pm x_o$ by infinite potential barriers. This implies that the wave functions vanish for $|x| \geq x_o$. The Schrödinger equation of this system is then:

$$-\frac{\hbar^2}{2m_o}\frac{d^2\Psi}{dx^2} + \frac{1}{2}m_o\omega_o^2x^2\Psi = W\Psi \qquad \text{(IV:1)}$$

where m_o is the mass of the oscillating particle and ω_o is the angular frequency of the isolated oscillator. The wave function $\Psi(x)$ in (IV:1) is subjected to boundary conditions:

$$\Psi(-x_o) = \Psi(x_o) = 0 \qquad \text{(IV:2)}$$

To solve (IV:1), subject to condition (IV:2), we first transform the equation into a dimensionless form. Thus by letting:[†]

$$y = \sqrt{\frac{2m_o\omega_o}{\hbar}}\,x \qquad \text{(IV:3)}$$

[†] Note that the inverse scale length given by (IV:3) is $\sqrt{2}$ times larger than usually defined in text books dealing with the S.H.O.

and

$$w = W/\hbar\omega_o \qquad \text{(IV:4)}$$

(IV:1) becomes

$$-\frac{d^2\Psi}{dy^2} + V(y)\Psi = w\Psi \qquad \text{(IV:5)}$$

where:

$$V(y) = \left(\frac{y}{2}\right)^2 \qquad \text{(IV:6)}$$

To solve (IV:5) numerically, the difference-quotient approximation is to be used for approximating $\frac{d^2\Psi}{dy^2}$ or $\Psi''(y)$. To accomplish this, we select an integer $N > 0$ and divide the interval $[-Y_o, Y_o]$ into N+1 equal subintervals whose end points are the meshpoints. Defining

$$Y_o = \sqrt{\frac{2m\omega_o}{\hbar}}\; x_o \qquad \text{(IV:7)}$$

we let:

$$y_i = -Y_o + ih, \qquad \text{for } i=0 \text{ to } N+1 \qquad \text{(IV:8)}$$

where

$$h = \frac{Y_o - (-Y_o)}{N+1} = \frac{2Y_o}{N+1} \qquad \text{(IV:9)}$$

At the interior meshpoints, y_i, $l = 1,2,....,N$, the differential equation to be approximated is

$$-\Psi''(y_i)+V(y_i)\Psi(y_i) = w\Psi(y_i) \qquad \text{(IV:10)}$$

Now, expanding the wave function $\Psi(y)$ up to cubic terms in a Taylor polynomial about the point y_i evaluated at y_{i+1} and y_{i-1}, we have:

$$\Psi(y_{i+1})=\Psi(y_i+h)=\Psi(y_i)+h\Psi(y_i)+\frac{h^2}{2}\Psi''(y_i)+\frac{h^3}{6}\Psi^3(y_i)+\frac{h^4}{24}\Psi^{(4)}(y_i) \qquad \text{(IV:11)}$$

for some point ξ_i^+, $y_i < \xi_i^+ < y_{i+1}$, and

$$\Psi(y_{i-1})=\Psi(y_i-h)=\Psi(y_i)-h\Psi(y_i)+\frac{h^2}{2}\Psi''(y_i)-\frac{h^3}{6}\Psi^3(y_i)+\frac{h^4}{24}\Psi^4(y_i) \qquad \text{(IV:12)}$$

for some point ξ_i^-, $y_{i-1} < \xi_i^- < y_i$.

If these two equations are added together, there results:

$$\Psi''(y_i) = \frac{\Psi(y_{i-1})-2\Psi(y_i)+\Psi(y_{i+1})}{h^2} - \frac{h^2}{24}\left[\Psi^{(4)}(\xi_i^+)+\Psi^{(4)}(\xi_i^-)\right] \qquad \text{(IV:13)}$$

Making use of Intermediate Value Theorem, the equation (IV:13) becomes

$$\Psi''(y_i) = \frac{\Psi(y_{i-1})-2\Psi(y_i)+\Psi(y_{i+1})}{h^2} - \frac{h^2}{12}\Psi^{(4)}(\xi_i) \qquad \text{(IV:14)}$$

for some point ξ_i, $y_{i-1} < \xi_i < y_{i+1}$.

Equation (IV:14) is called the Central Difference Formula for $\Psi''(y_i)$. Assuming that h is a small number such that the last term in Eq. (IV:14) can be neglected, and bearing in mind that the truncation error is of $O(h^2)$, we thus have:

$$\Psi(y_i) = \frac{\Psi(y_{i-1})-2\Psi(y_i)+\Psi(y_{i+1})}{h^2} \qquad \text{(IV:15)}$$

Replacing $\Psi''(y_i)$ in (IV:10) by (IV:15) the differential equation is approximated by the difference equation:

$$-\left[\frac{\Psi(y_{i-1})-2\Psi(y_i)+\Psi(y_{i+1})}{h^2}\right] + V(y_i)\Psi(y_i) = w\Psi(y_i) \qquad \text{(IV:16)}$$

for each i = 1,2,3,...,N, and subject to boundary conditions:

$$\Psi(Y_o) = \Psi(Y_o) = 0 \text{ or } \Psi(y_o) = \Psi(y_{n+1}) = 0 \qquad \text{(IV:17)}$$

Equation (IV:16) can be rewritten as

$$
\begin{aligned}
-\frac{1}{h^2}\Psi(y_o)+\left\{\frac{2}{h^2}+V(y_1)\right\}\Psi(y_o)-\frac{1}{h^2}\Psi(y_2) &= w\Psi(y_1)\\
-\frac{1}{h^2}\Psi(y_1)+\left\{\frac{2}{h^2}+V(y_2)\right\}\Psi(y_2)-\frac{1}{h^2}\Psi(y_3) &= w\Psi(y_2)\\
&\vdots\\
-\frac{1}{h^2}\Psi(y_{N-1})+\left\{\frac{2}{h^2}+V(y_N)\right\}\Psi(y_N)-\frac{1}{h^2}\Psi(y_{N+1}) &= w\Psi(y_N)
\end{aligned}
\tag{IV:18}
$$

Substituting (IV:17) into the first and the last equations of (IV:18) we get:

$$
\begin{aligned}
\left\{\frac{2}{h^2}+V(y_1)\right\}\Psi(y_1)-\frac{1}{h^2}\Psi(y_2) &= w\Psi(y_1)\\
-\frac{1}{h^2}\Psi(y_1)+\left\{\frac{2}{h^2}+V(y_2)\right\}\Psi(y_2)-\frac{1}{h^2}\Psi(y_3) &= w\Psi(y_2)\\
&\vdots\\
-\frac{1}{h^2}\Psi(y_{N-1})+\left\{\frac{2}{h^2}+V(y_N)\right\}\Psi(y_N) &= w\Psi(y_N)
\end{aligned}
\tag{IV:19}
$$

Equation (IV:18) can be expressed in the tridiagonal N x N-matrix form shown in Eq. (IV:20):

$$\begin{bmatrix} \frac{2}{h^2}+V(y_1) & -\frac{1}{h^2} & 0 & \cdots & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2}+V(y_2) & -\frac{1}{h^2} & \ddots & \vdots \\ 0 & -\frac{1}{h^2} & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & -\frac{1}{h^2} \\ 0 & \cdots & 0 & -\frac{1}{h^2} & \frac{2}{h^2}+V(y_N) \end{bmatrix} \begin{bmatrix} \Psi(y_1) \\ \Psi(y_2) \\ \vdots \\ \Psi(y_N) \end{bmatrix} = w \begin{bmatrix} \Psi(y_1) \\ \Psi(y_1) \\ \vdots \\ \Psi(y_N) \end{bmatrix} \tag{IV:20}$$

or $W\psi = w\Psi$ where the matrix A, shown in Eq. (IV:20) is also a a symmetrical. From mathematics, we know that it is possible to diagonalize the above matrix without changing its eigenvalues. The matrix which transforms A to diagonal form is called a similarity transformation. Here the process of diagonalization is done by computer. The computer program for this process is given in *Appendix A*. The well known QR algorithm for calculating the eigenvalues of the tridiagonal and symmetry matrix is used in this computation (see Burden et al. [32]). The diagonal matrix obtained above represents the eigenvalues (eigen-energies) of the matrix A, since $A\Psi = w\Psi$ or

$$\begin{bmatrix} A_1 & 0 & 0 & \cdots & 0 \\ 0 & A_2 & 0 & \ddots & \vdots \\ 0 & 0 & A_3 & \ddots & \vdots \\ \vdots & 0 & 0 & \ddots & 0 \\ 0 & \cdots & \cdots & 0 & A_N \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_N \end{bmatrix} = w \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_N \end{bmatrix} \qquad \text{(IV:21)}$$

It should be noted that the size of the matrix is determined by the integer N, and N is selected so that the distance $h = \frac{2Y_o}{N+1}$ between y_2 and y_{i+1} is very small. Of course, this distance can be made as small as we wish. In other words, N can be chosen as large as we want. When N is large, the size of the matrix is also large, meaning more computation time is required to compute the eigenvalues of the matrix. In order to speed up the computation time, one has to choose N so that the distance $h = \frac{2Y_o}{N+1}$ is reasonably small and the truncation error is also small. Of course, the larger the interval $[-Y_o, Y_o]$, the bigger the value of N to be chosen.

Now, we use the eigenvalue which is obtained by the QR algorithm to compute its corresponding eigenvector (wave function), of course, the wave function which is obtained above is not entirely accurate since its corresponding eigenvalue carries a rounding error which is due to iteration in the QR algorithm. To find the nearly exact eigenvalue and eigen-vector, we write a computer program in which we can calculate this nearly exact eigen-energy and wave function* simultaneously. This program is given in *Appendix B*.

The computed energies and wave functions are shown in Figs. 8 to 14 for Y_o in the range $2 \sim 5$. In argon this corresponds to the density range 802 am ($Y_o=2$) to 51.3 am ($Y_o=5$), with a similar density range for most other gases. Note here that energies are quoted in units of $\hbar\omega_o$ and that the energy and wave functions of the isolated oscillator are shown as dashed lines.

As mentioned in Sec. III:b:ii, we are not able to solve the Schrödinger equation given by (III:51) in an exact manner. Instead we introduce perturbation theory, that is, we assume the macroscopic field, E, so small that qEx can be treated as a perturbation. Now, let us consider that the unperturbed system is a restricted simple harmonic oscillator without dipolar interaction with a wave equation given by (IV:1) and subject to boundary conditions. The

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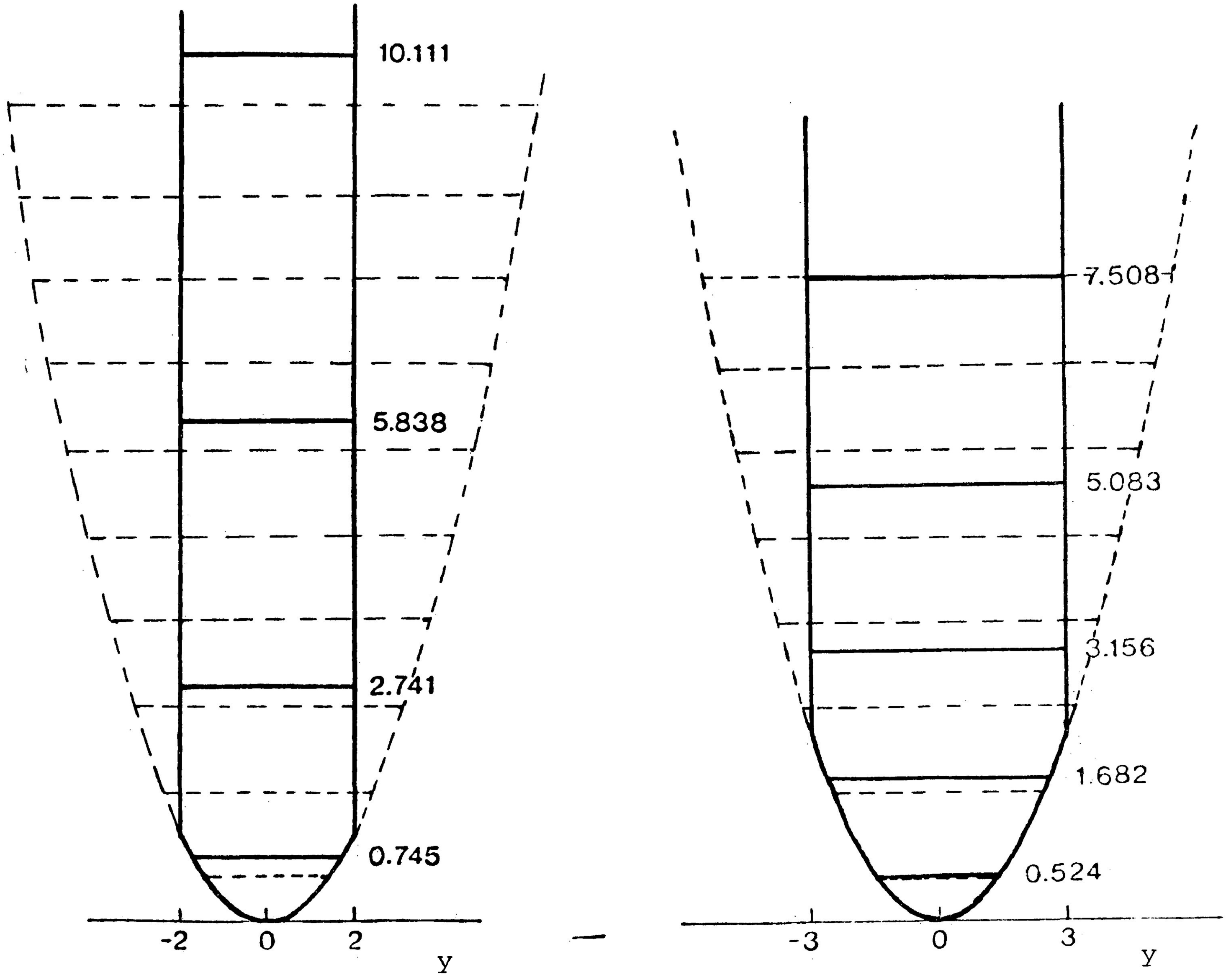
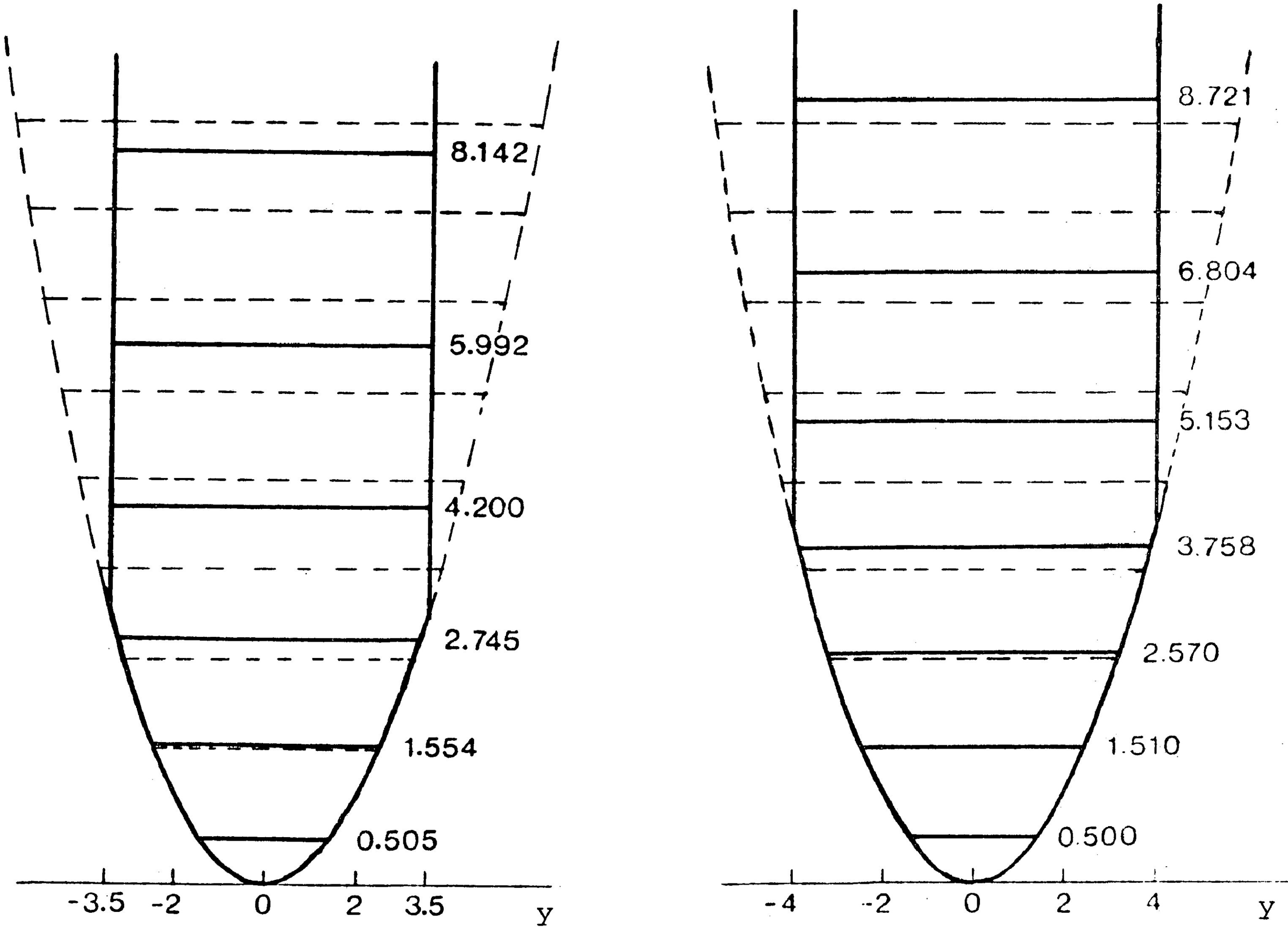
**Appendix D* gives a programme for checking the accuracy of the wave function and energy. The former is seen to be correct to within 1 part in 10^6.



$Y_o = 2$ $Y_o = 3$

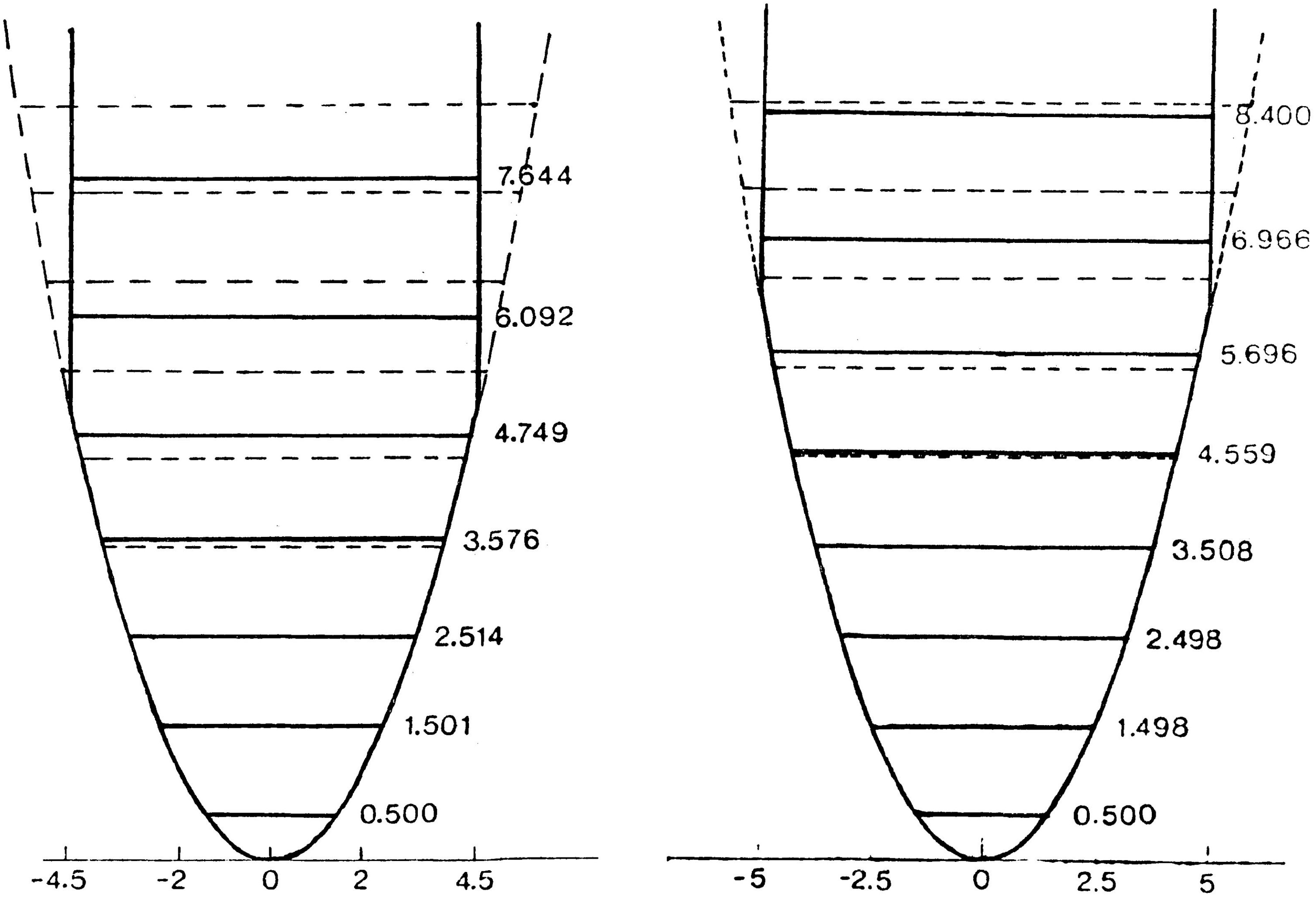
FIG. 8a: Energy levels of restricted S.H.O. for $Y_o = 2,3$.



$Y_o = 3.5$

$Y_o = 4$

FIG. 8b: Energy levels of restricted S.H.O. for $Y_o = 3.5$ and 4.



$Y_o = 4.5$ $Y_o = 5$

FIG. 8c: Energy levels of restricted S.H.O. for $Y_o = 4.5$ and 5.

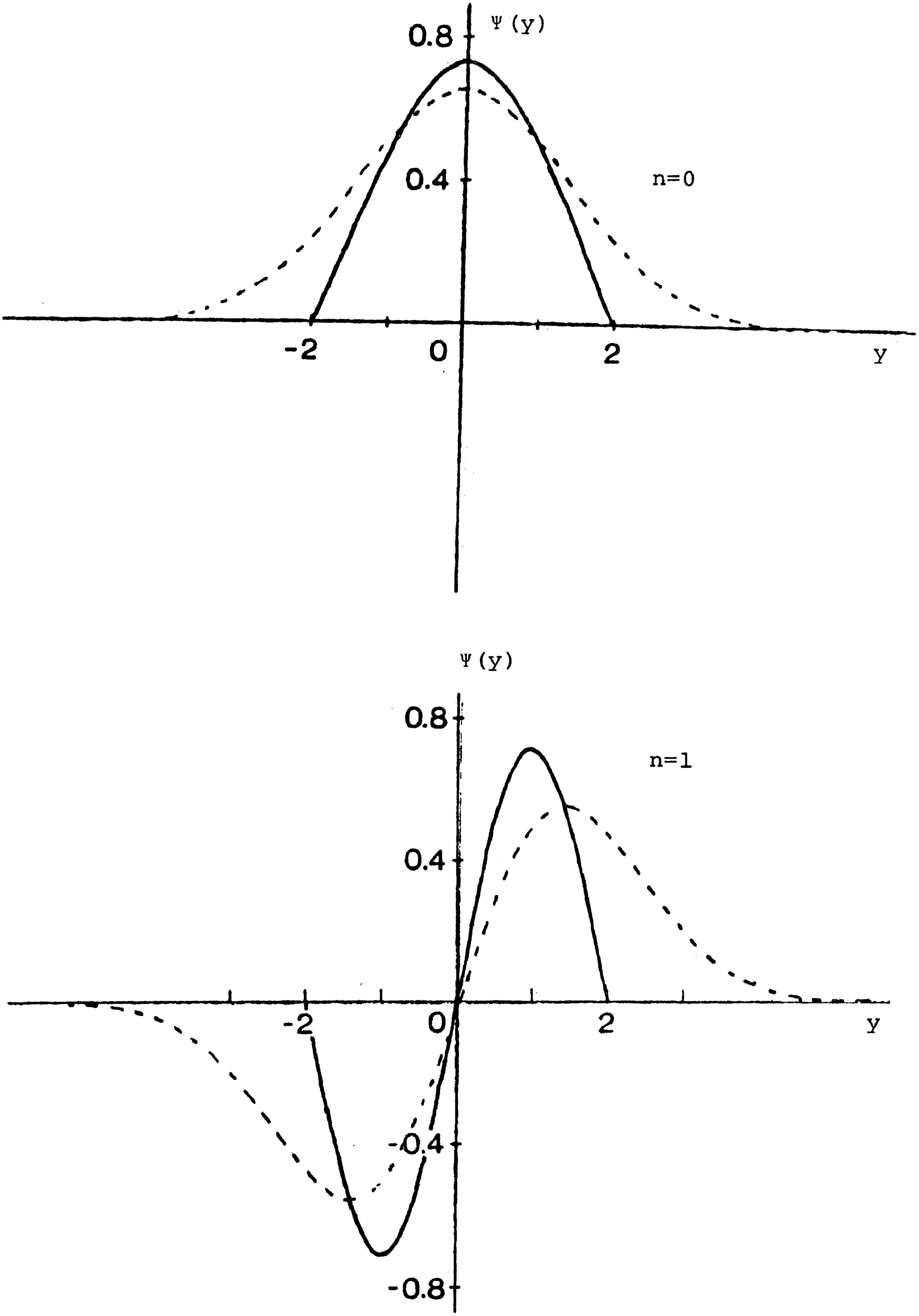


FIG. 9a: Wave functions of restricted S.H.O. for $Y_o = 2$.

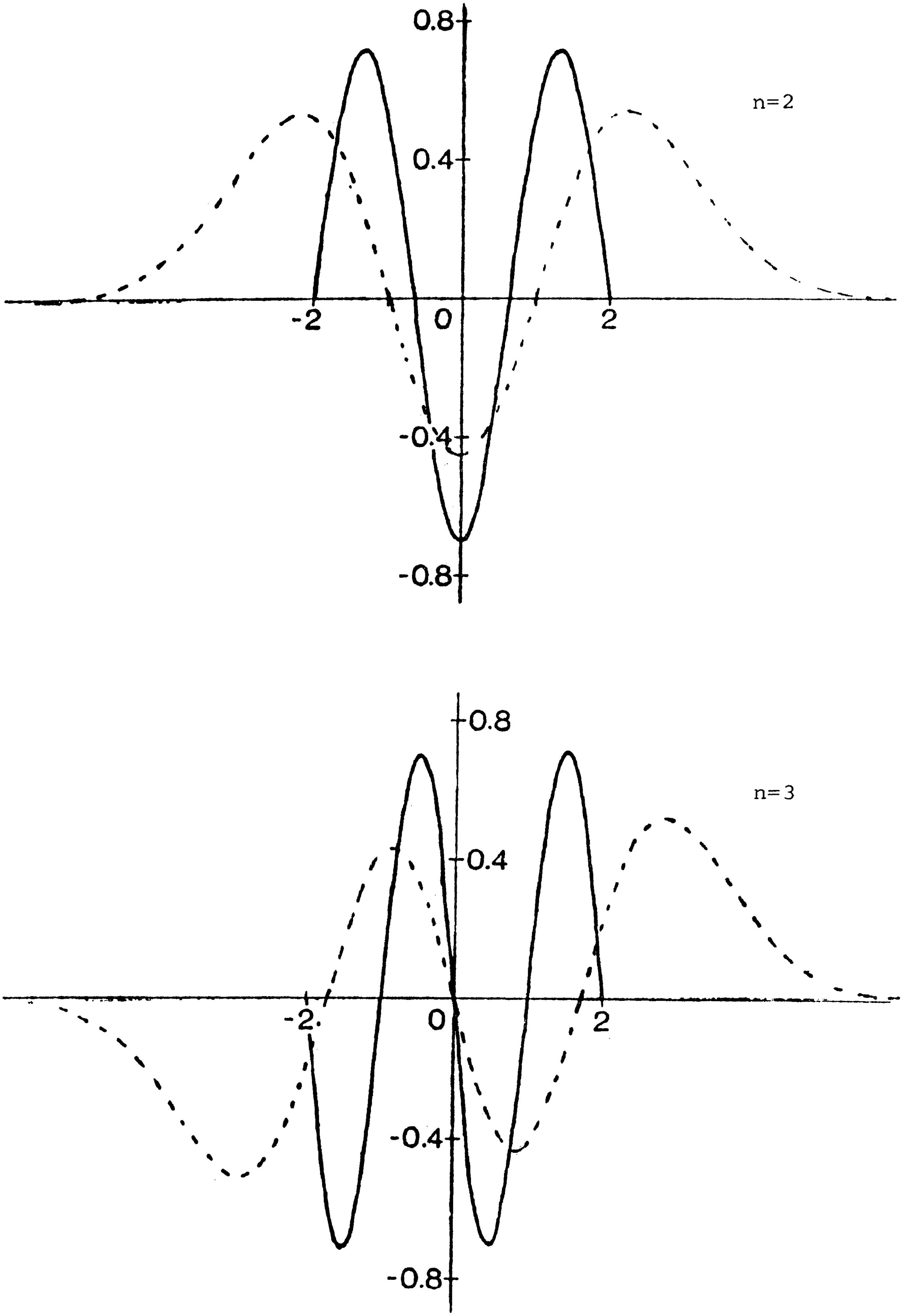


FIG. 9b: Wave functions of restricted S.H.O. for $Y_o = 2$.

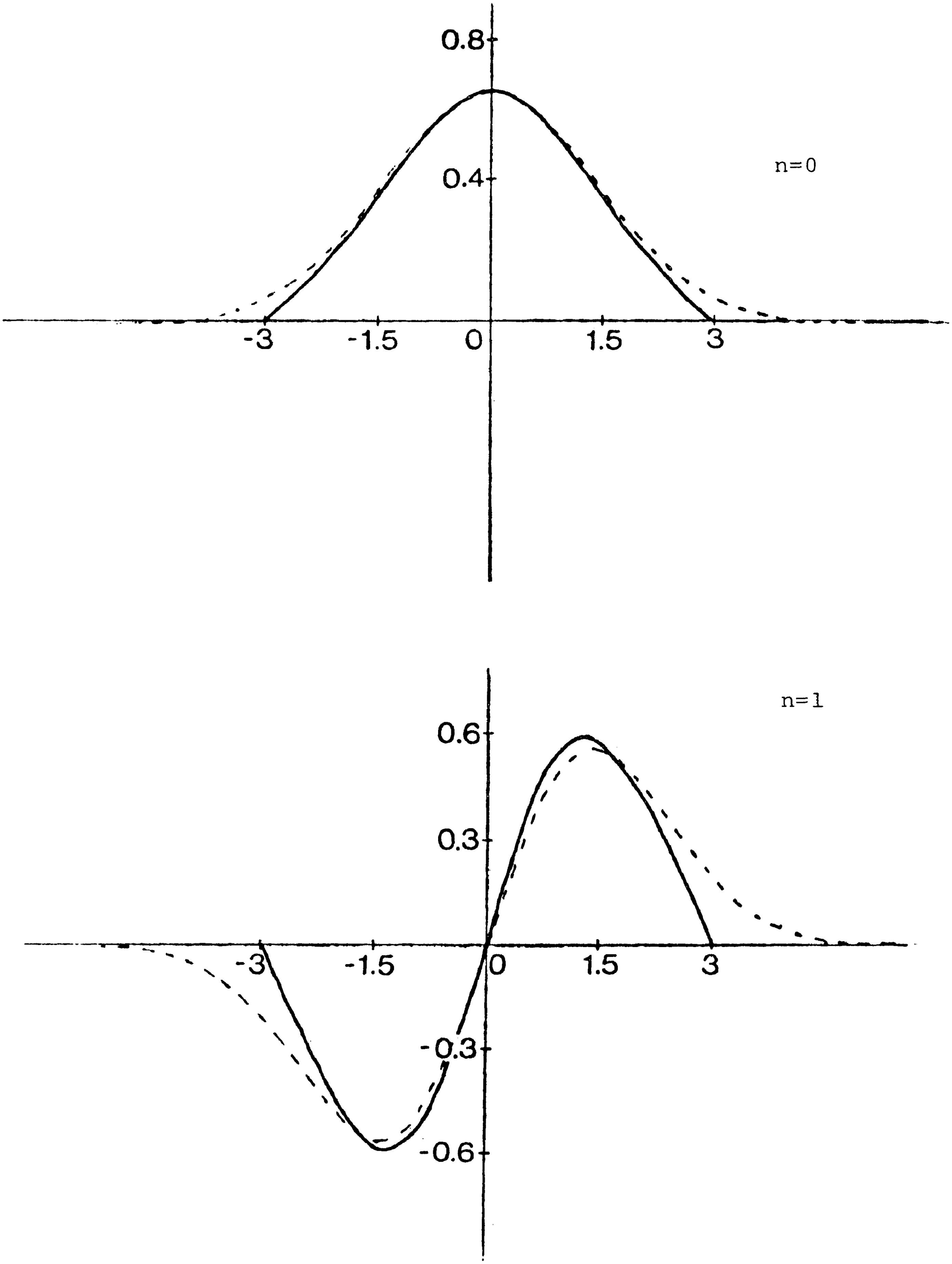


FIG. 10a: Wave functions of restricted S.H.O. for $Y_o = 3$.

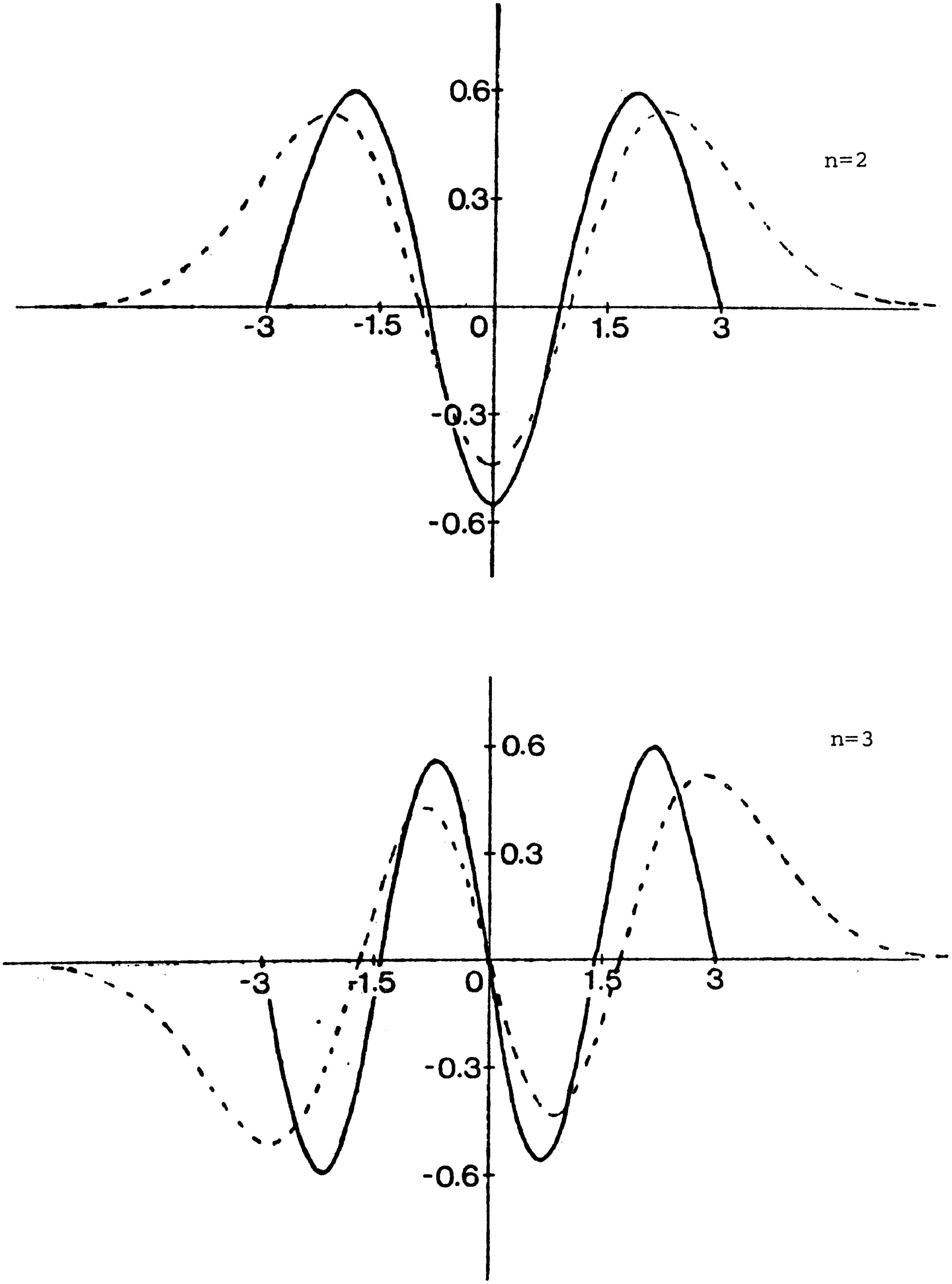


FIG. 10b : Wave functions of restricted S.H.O. for $Y_o = 3$.

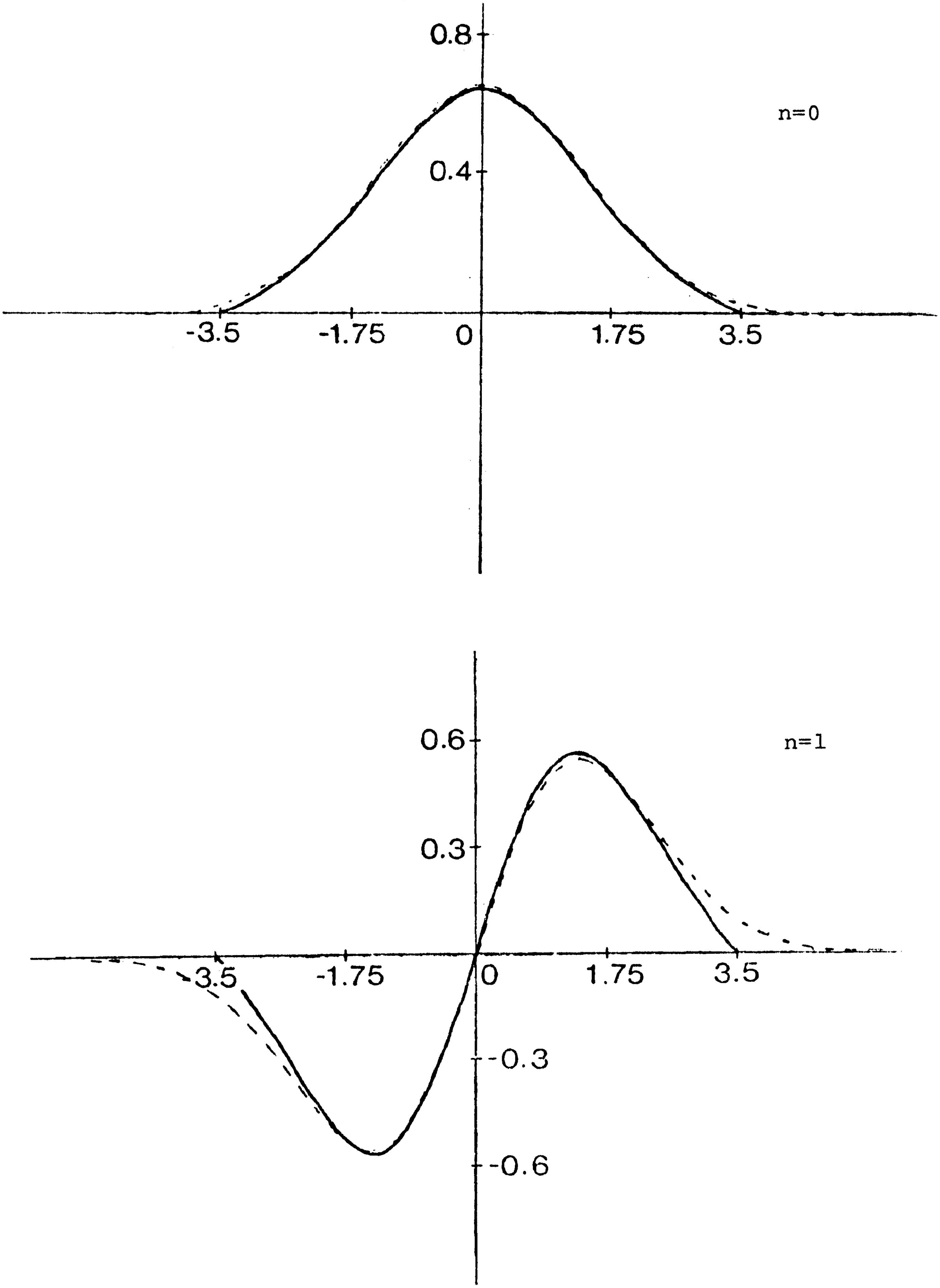


FIG. 11a: Wave functions of restricted S.H.O. for $Y_o = 3.5$.

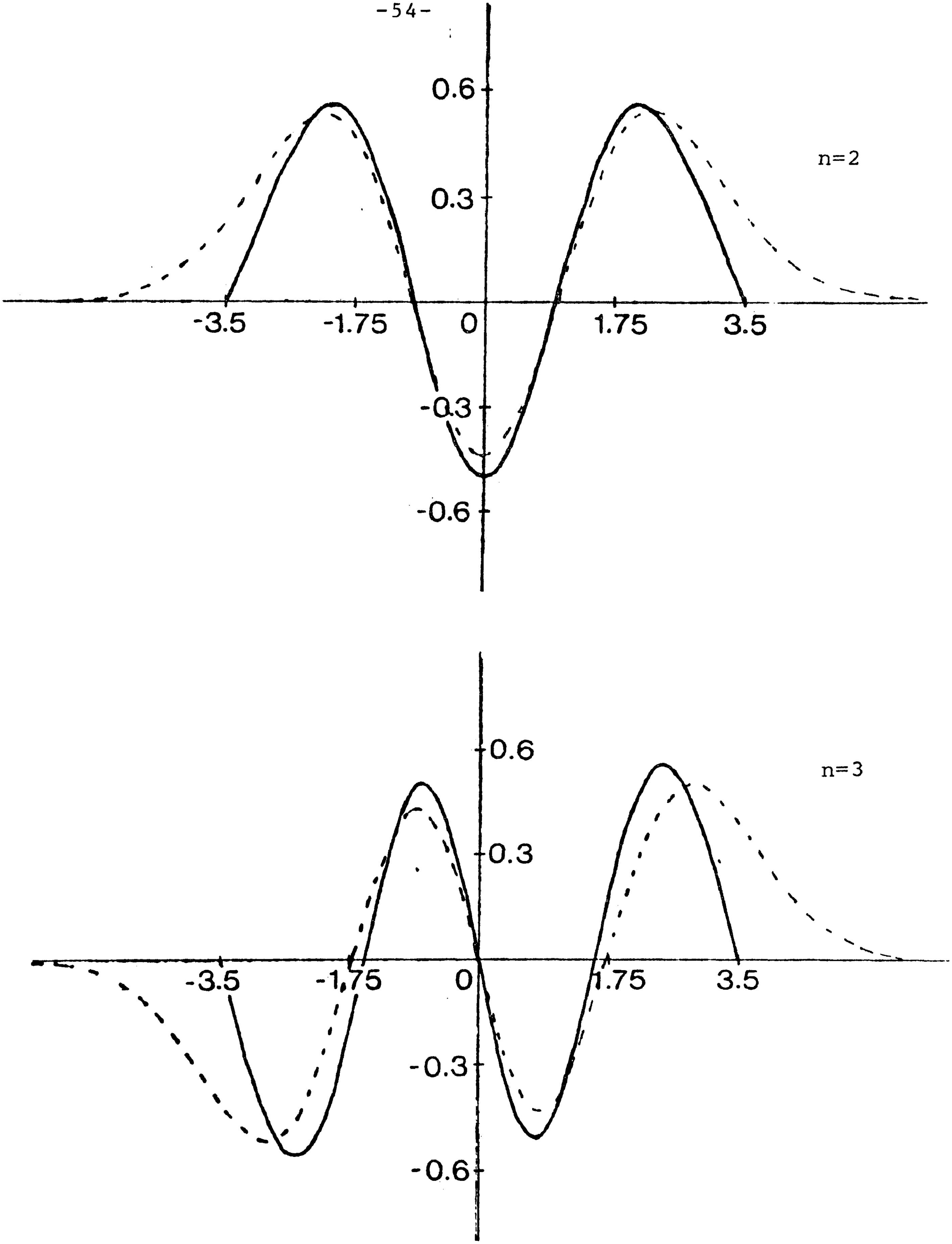


FIG. 11b: Wave functions of restricted S.H.O. for $Y_o = 3.5$.

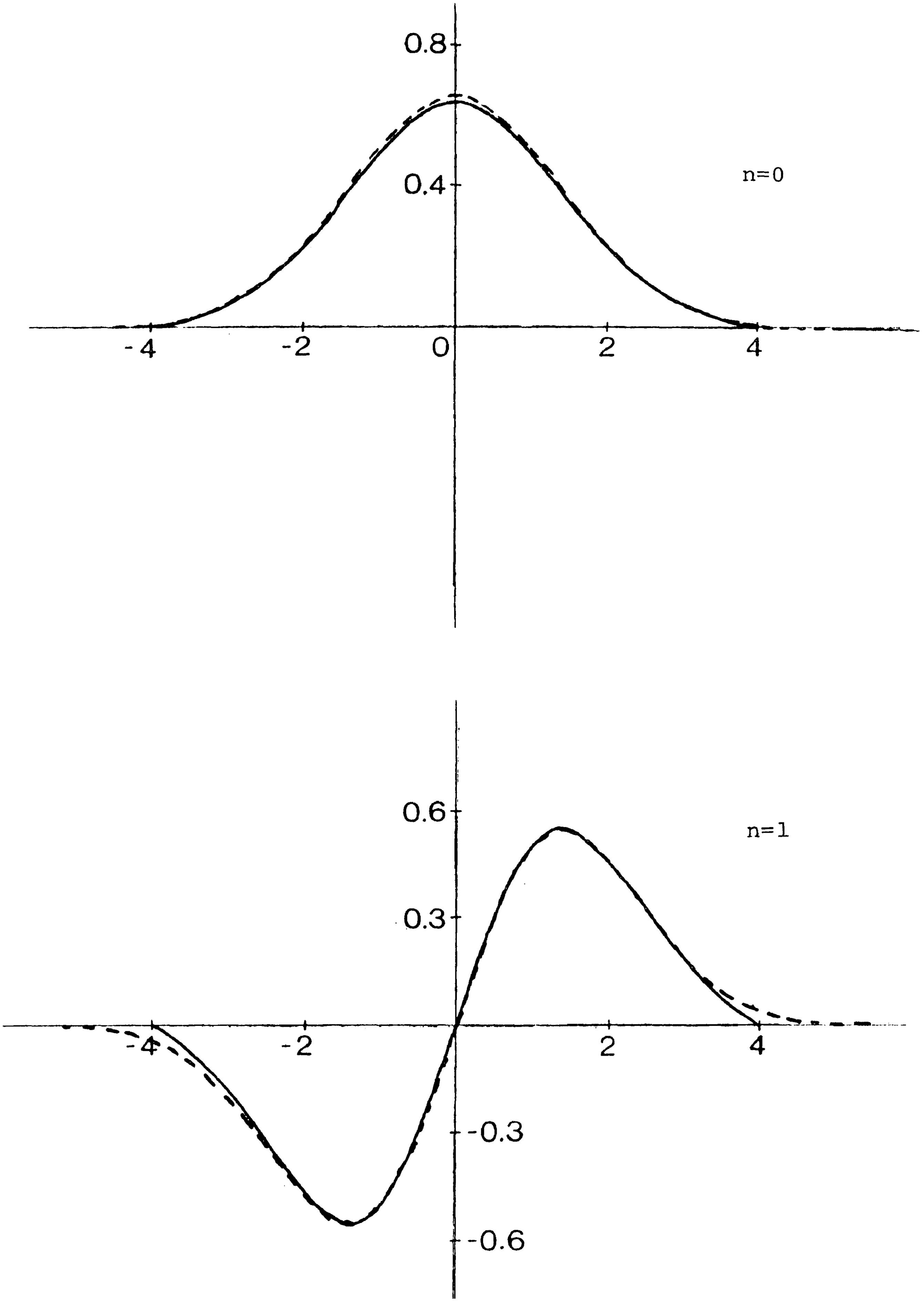


FIG. 12a: Wave functions of restricted S.H.O. for $Y_o = 4$.

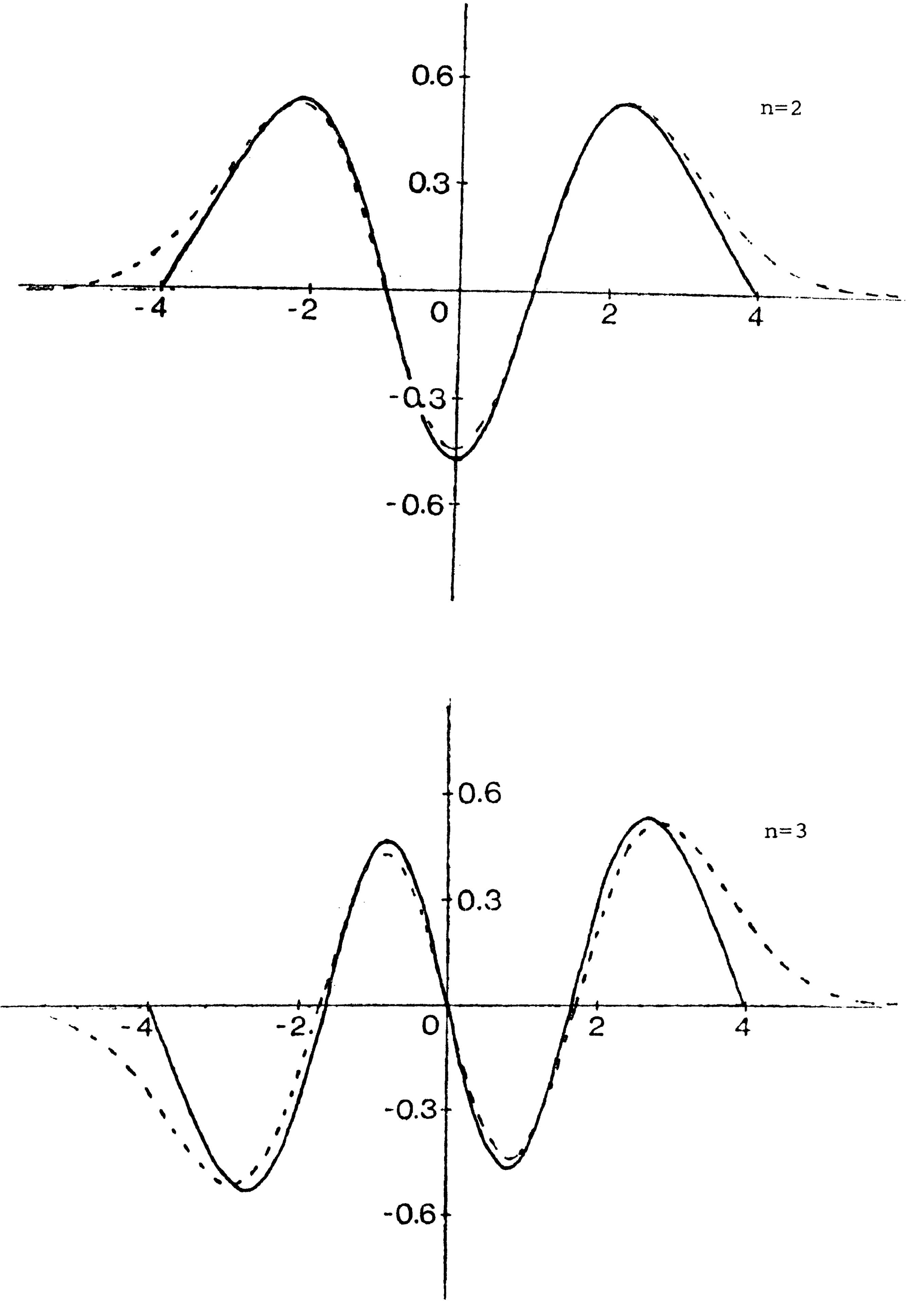


FIG. 12b: Wave functions of restricted S.H.O. for $Y_o = 4$.

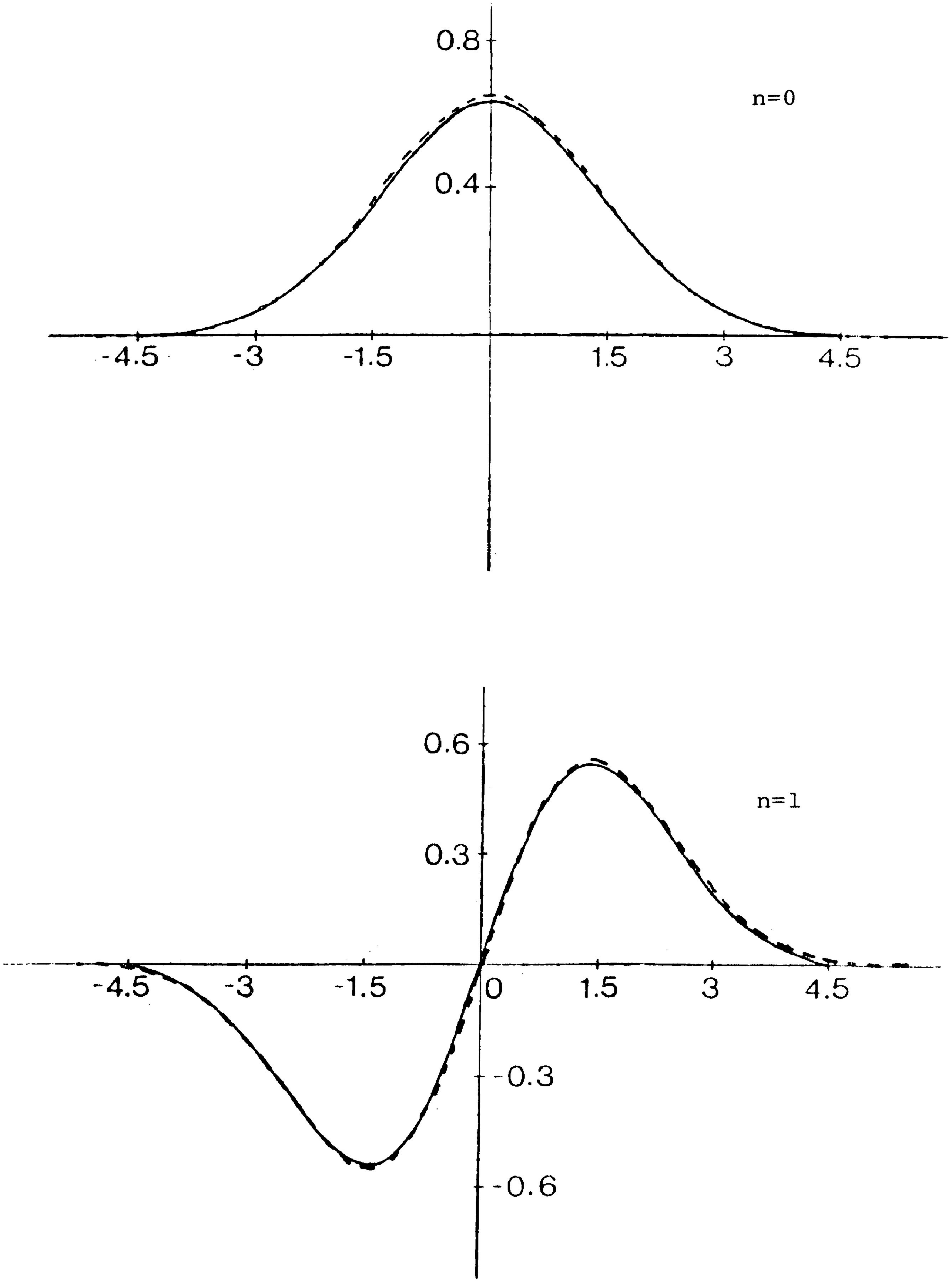


FIG. 13a: Wave functions of restricted S.H.O. for $Y_o = 4.5$.

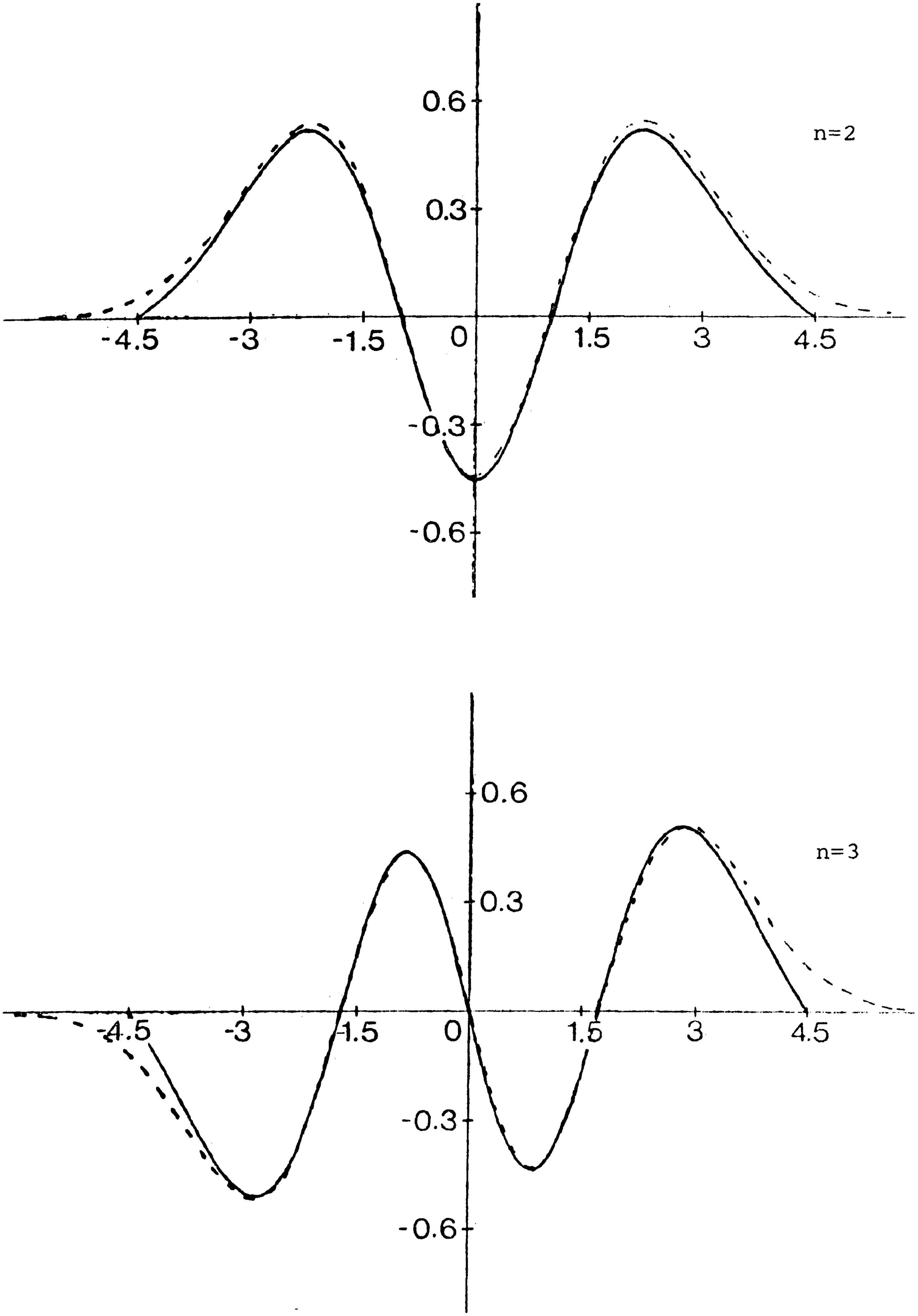


FIG. 13b: Wave function of restricted S.H.O. for $Y_o = 4.5$.

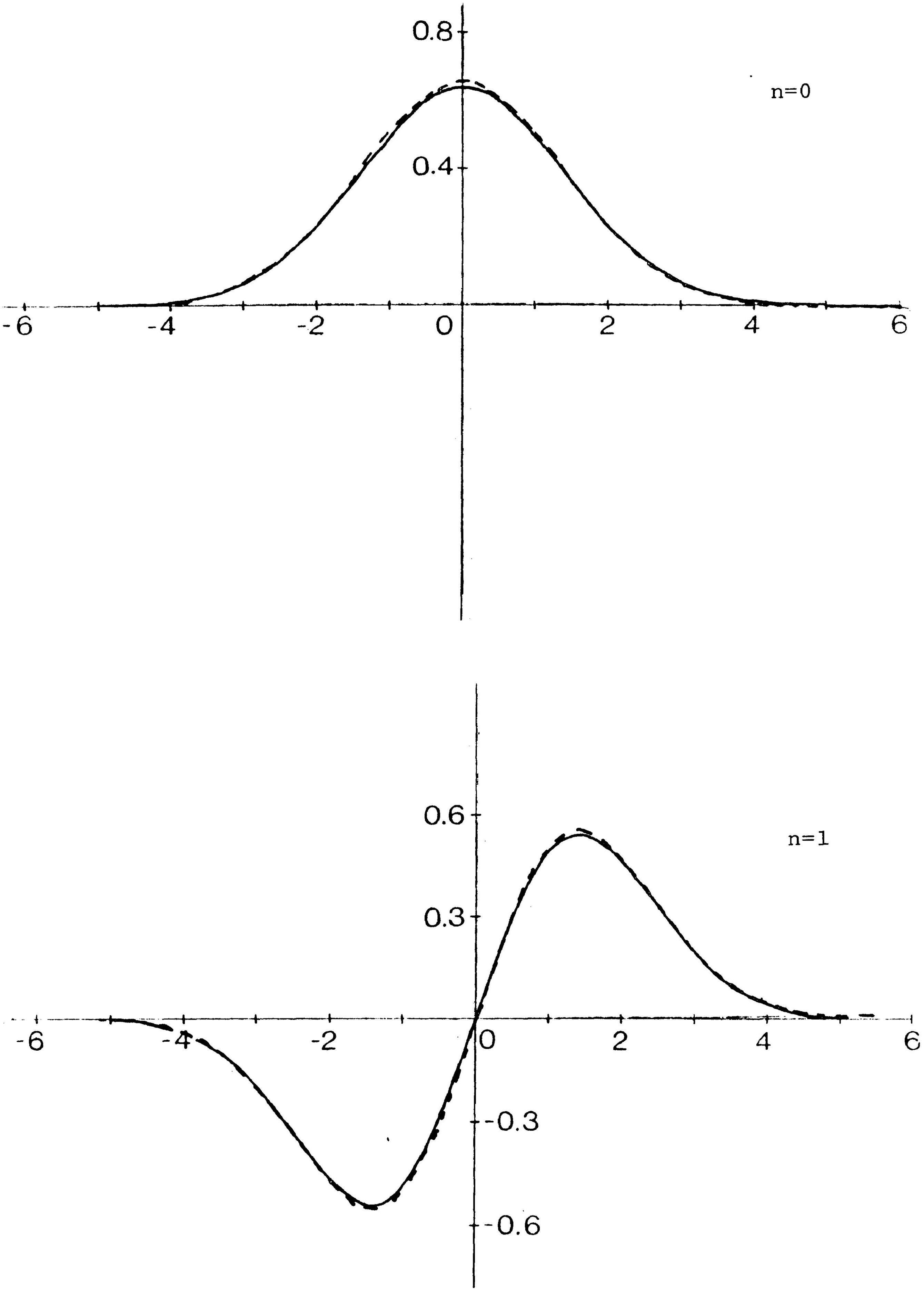


FIG. 14a: Wave function of restricted S.H.O. for $Y_o = 5$.

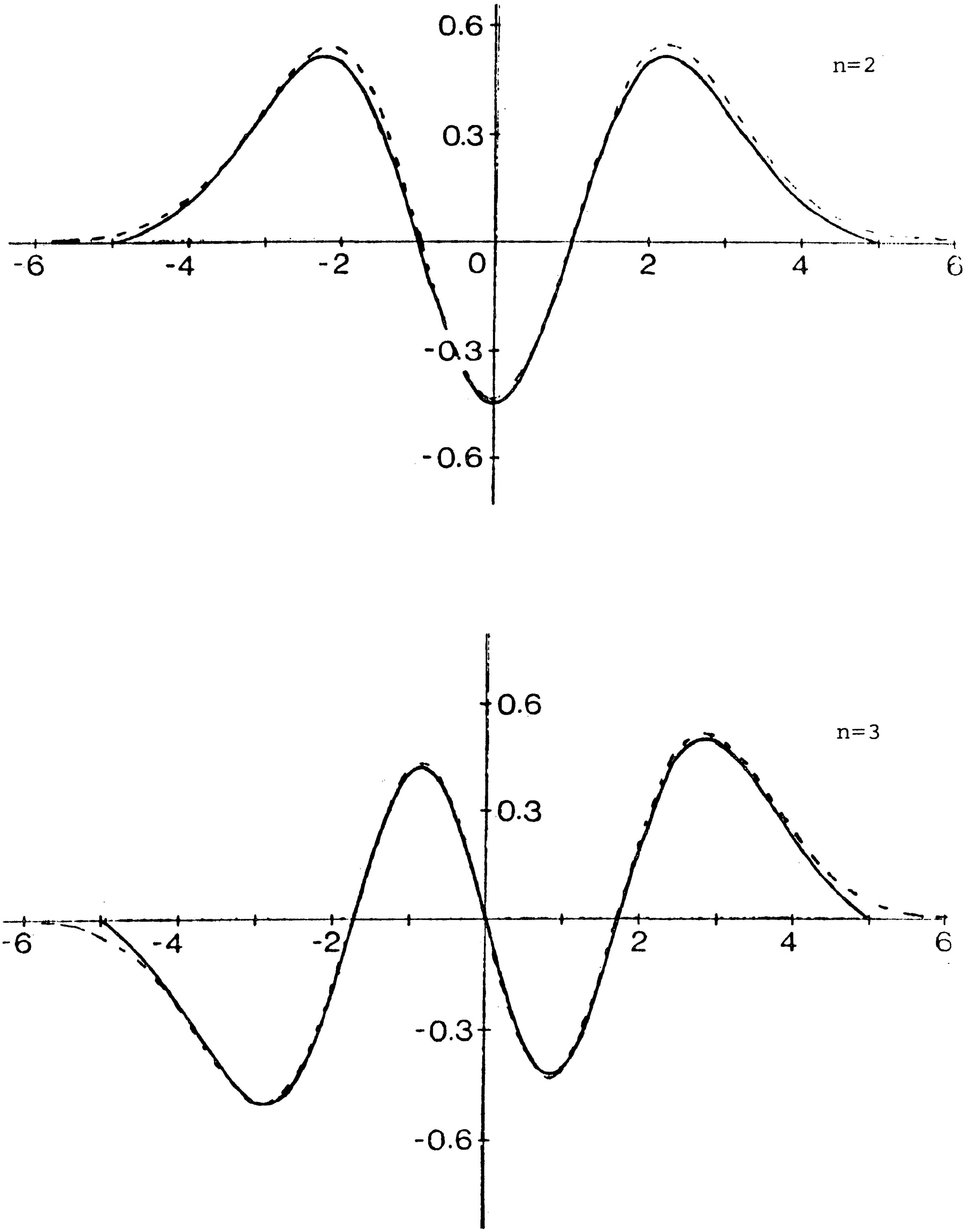


FIG. 14b: Wave function of restricted S.H.O. for $Y_o = 5$.

Hamiltonian of this system will be:

$$H = -\frac{\hbar^2}{2m_o}\frac{d^2}{dx^2} + \frac{1}{2}m_o\omega_o^2 x^2 - qEx = H_o qEx \qquad \text{(IV:22)}$$

According to the perturbation theory, the change in energy is given by::

$$W = W_o + qE\langle\Psi_o|x|\Psi_o\rangle + \sum_{n\neq 0}^{\infty}\frac{|\langle\Psi_n|x|\Psi_o\rangle|^2}{W_o - W_n}\, q^2E^2 \qquad \text{(IV:23)}$$

where W_n and $\Psi_n(x)$ are the energy and the wave function of the unperturbed state of the restricted oscillator without dipolar interaction. The matrix element $\langle\Psi_o|x|\Psi_o\rangle$ is equal to zero since $\Psi_o(x)$ has even or odd parity. Therefore (IV:23) can be simplified. It becomes:

$$W = W_o - \sum_{n\neq 0}^{\infty}\frac{|\langle\Psi_n(x)|x|\Psi_o(x)\rangle|^2}{W_n - W_o}\, q^2E^2 \qquad \text{(IV:23)}$$

The static polarizability of the restricted oscillator without dipolar interaction is given by:

$$\alpha = -\frac{\partial^2 W}{\partial E^2} = 2q^2\sum_{n\neq 0}^{\infty}\frac{|\langle\Psi_n(x)|x|\Psi_o(x)|^2}{W_n - W_o} \qquad \text{(IV:25)}$$

The wave functions, which are calculated by computer, are functions of y, where y is defined by (IV:3) The normalization of wave function $\Psi(y)$ is done by computer (see *Appendix B*) and given by:

$$\int_{-Y_o}^{Y_o} \Psi(y)\Psi(y)dy = 1 \tag{IV:26}$$

However, the normalization of wave function $\Psi(x)$ is

$$\int_{-x_o}^{x_o} \Psi(x)\Psi(x)dx = 1 \tag{IV:27}$$

Using (IV:3), (IV:27) becomes

$$\sqrt{\frac{\hbar}{2m_o\omega_o}} \int_{-Y_o}^{Y_o} \Psi(x)\Psi(x)dy = 1 \tag{IV:28}$$

Comparing (IV:26) with (IV:28) yields:

$$\Psi(x) = \left(\frac{2m_o\omega_o}{\hbar}\right)^{\frac{1}{4}} \Psi(y) \tag{IV:29}$$

Using (IV:29), (IV:3) and (IV:4) in (IV:25) the polarizability of a restricted oscillator without dipolar interaction then becomes:

$$\alpha = \frac{q^2}{m_o\omega_o{}^2}\sum_{n=1}^{\infty}\frac{|<\Psi_n(y)|y|\Psi_o(y)>|^2}{w_n-w_o} \tag{IV:30}$$

Defining $\alpha_o = q^2/m_o\omega_o{}^2$ (IV:30) gives the relative polarizability:

$$\frac{\alpha}{\alpha_o} = \sum_{n=1}^{\infty}\frac{|<\Psi_n(y)|y|\Psi_o(y)>|^2}{w_n-w_o} \tag{IV:31}$$

Because the excited state wave functions have more nodes, the value of the matrix dipole element $<\Psi_n|y|\Psi_o>$ is very small for n>1. Thus, the relative polarizability can be approximated and is given here for the first 8 terms only, viz:

$$\frac{\alpha}{\alpha_o} = \sum_{n=1}^{8}\frac{|<\Psi_n(y)|y|\Psi_o(y)>|^2}{w_n-w_o} \tag{IV:32}$$

We compute (IV:32) using the energies w_n and wave functions $\Psi_n(y)$ computed above. The program for this calculation is given in *Appendix C*. The relative polarizability of a restricted simple harmonic oscillator without dipolar interaction vs. density is shown in Fig. 15. Here the density is calculated assuming $N_o = (2x_o)^{-3}$.

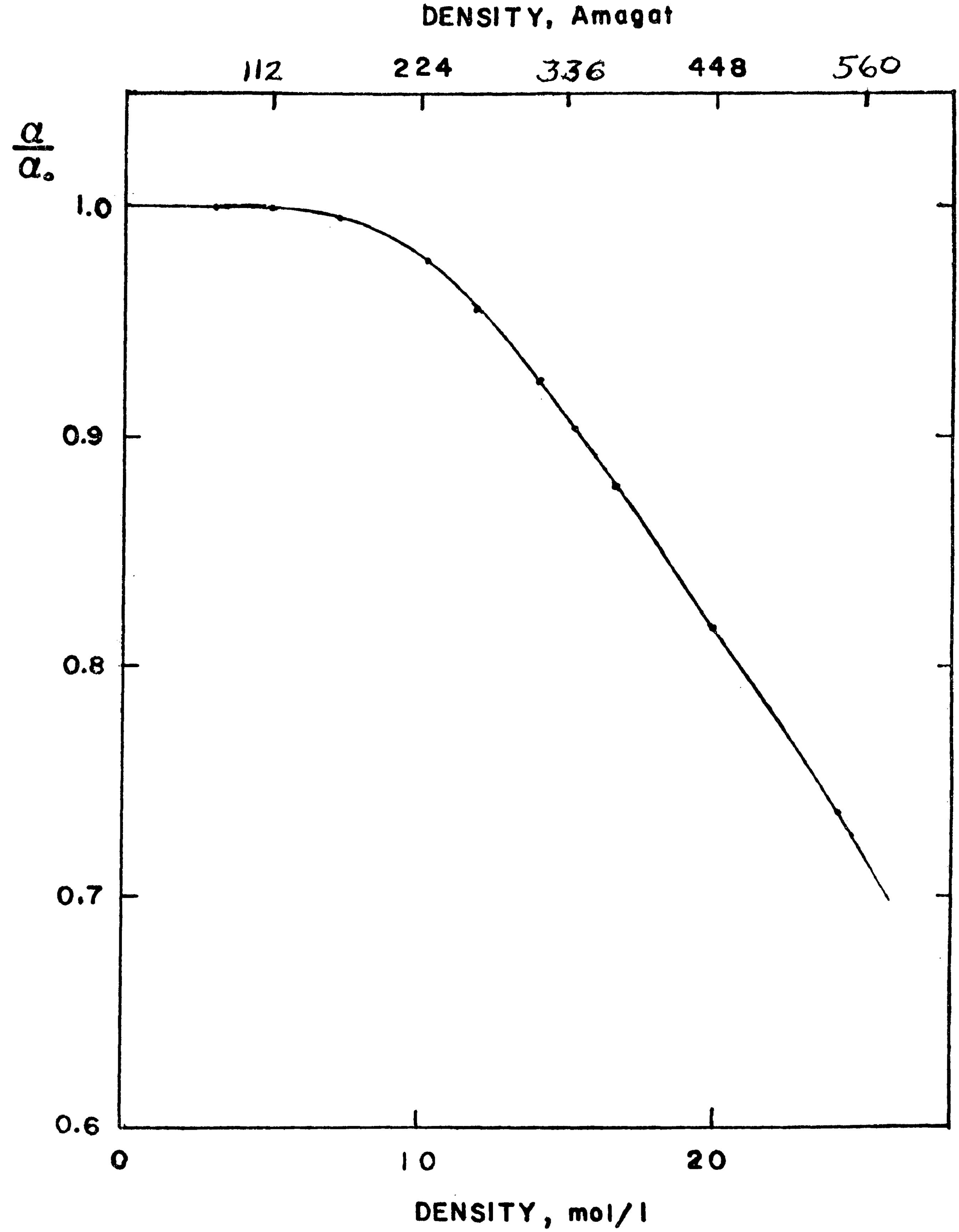


FIG. 15: Ground state polararization of restricted S.H.O. as a function of density.

V. COMPUTED ENERGIES, WAVE FUNCTIONS AND STATIC POLARIZABILITY OF THE RESTRICTED SIMPLE HARMONIC OSCILLATOR WITH DIPOLAR INTERACTION

The Hamiltonian of the restricted simple harmonic oscillator in the absence of macroscopic field, E, but with dipolar interaction present is given by:

$$H = -\frac{\hbar^2}{2m_o}\frac{d^2}{dx^2} + \frac{1}{2} m_o \omega_{eff}^2 x^2$$

and the Schrödinger equation of this system is thus:

$$H\Psi = W\Psi$$

or

$$-\frac{\hbar^2}{dm_o}\frac{d^2\Psi}{dx^2} + \frac{1}{2} m_o \omega_{eff}^2 x^2 \Psi = W\Psi \qquad (V:1)$$

or

$$-\frac{\hbar^2}{2m_o}\frac{d^2\Psi}{dx^2} + \frac{1}{2} m_o \omega_o^2 x^2 \left(1 - \frac{\omega_p^2}{\omega_o^2}\right)\Psi = W\Psi \qquad (V:2)$$

Subjected to boundary condition:

$$\Psi(-x_o) = \Psi(x_o) = 0 \qquad (V:3)$$

Since we have basically the same problem as in Sec. IV, but with a different effective frequency in the potential, we use the same method of solution subject to boundary conditions (V:3). Now, let us introduce the dimensionless y and w given by (IV:3) and (IV:4), viz:

$$y = \sqrt{\frac{2m_o\omega_o}{\hbar}}\; x \tag{V:4}$$

and

$$w = W/\hbar\omega_o \tag{V:5}$$

(V:2) becomes

$$-\frac{d^2\Psi}{dy^2} + V(y)\Psi = w\Psi \tag{V:6}$$

where now:

$$V(y) = \left(\frac{y}{2}\right)^2 \left[1 - \frac{\omega_p{}^2}{\omega_o^2}\right] \tag{V:7}$$

and the wave function $\Psi(y)$ is still subject to the boundary conditions:

$$\Psi(-Y_o) = \Psi(Y_o) = 0 \tag{V:8}$$

where

$$Y_o = \sqrt{\frac{2m_o\omega_o}{\hbar}}\; x_o \tag{V:9}$$

Now, let us discretize (V:6) and replace $\frac{d^2\Psi}{dy^2}$ by (IV:14) and also bearing in mind that the truncation error is of $O(h^2)$. We thus have:

$$-\left[\frac{\Psi_{i-1}-2\Psi_i+\Psi_{i+1}}{h^2}\right] + V(y_i)\Psi_i = w\Psi_i \tag{V:10}$$

where:

$$h = \frac{2Y_o}{N+1} \tag{V:11}$$

and N is the number of interior points. Also:

$$y_i = Y_o + i \times h \quad \text{for } i=1,2,3,\ldots N. \tag{V:12}$$

By imposing boundary conditions (V:8), (V:10) is written in the compact form shown in Eq. (V:13) below:

$$\begin{bmatrix} \frac{2}{h^2}+V(y_1) & -\frac{1}{h^2} & 0 & \cdots & 0 \\ -\frac{1}{h^2} & \frac{2}{h^2}+V(y_2) & -\frac{1}{h^2} & \ddots & \vdots \\ 0 & -\frac{1}{h^2} & \ddots & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & -\frac{1}{h^2} \\ 0 & \cdots & 0 & -\frac{1}{h^2} & \frac{2}{h^2}+V(y_N) \end{bmatrix} \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_N \end{bmatrix} = w \begin{bmatrix} \Psi_1 \\ \Psi_2 \\ \vdots \\ \Psi_N \end{bmatrix} \tag{V:13}$$

To diagonalize the above matrix using the well known QR algorithm, one has to know the value of $V(y_i)$, for i=1,2,3....,N. According to (V:7), $V(y_i)$ depends on ω_p and ω_o. From (III:36) we have:

$$\omega_p^2 = \left(\frac{4\pi q^2 N_o}{m_o}\right) \qquad \text{(III:36)}$$

Now assume that the number density, N_o is equal to:

$$N_o = \frac{1}{(2x_o)^3} \qquad \text{(V:14)}$$

where the charge q is equal to e and the mass m_o is equal to electron rest mass m_e. Then (III:36) becomes

$$\omega_p^2 = \frac{4\pi e^2}{m_e(2x_o)^3} \qquad \text{(V:15)}$$

Using (V:9) the quantity $\frac{\omega_p^2}{\omega_o^2}$ is then given by:

$$\frac{\omega_p^2}{\omega_o^2} = \frac{\pi e^2}{Y_o{}^3}\sqrt{\frac{2m_e}{\omega_o h^3}} \qquad \text{(V:16)}$$

By assigning values to Y_o and using values of ω_o which are obtained by extrapolating the experimental Clausius-Mossotti functions $\frac{\varepsilon-1}{\varepsilon+2}\frac{W}{\rho} = \frac{4\pi}{3}A\alpha_o = \frac{4\pi}{3}A\frac{e^2}{m_o\omega_o{}^2}$ to zero density, one can evaluate $V(y_i)$ for $i=1,2,\ldots,N$. Using this procedure we find the frequencies of the electron in the isolated atoms to be for Argon $\omega_o = 1.243\text{x}10^{16}$ sec^{-1}; for Helium $\omega_o = 3.5115\text{x}10^{16}$ sec^{-1}; for Krypton $\omega_o = 1.009\text{x}10^{16}$ sec^{-1}, while for CO_2 $\omega_o = 0.9245\text{x}10^{16}$ sec^{-1}.

Since we now know the value of $V(y_i)$ the diagonalization of (V:13) can be performed. This process is, of course, done by computer. The program for assigning a value to Y_o and ω_o, and calculating the quantity $V(y_i)$, and also diagonalizing the matrix which is given by (V:13) is given in *Appendix A*. As mentioned in Sec. IV, the eigen-energies computed above are not entirely accurate. This may be caused by the iteration process used in the calculating of the eigenvalues. To find the nearly exact eigenvalues and eigenvectors, we write a program which can compute the nearly exact eigenvalues and eigenvectors simulaneously. This program is listed in *Appendix B*.

The computed eigen-energies and wave functions of Ar gas are shown in Figs. 16 to 20. Note that the energies and wave functions of the isolated oscillator are shown as dashed lines in all figures. It should also be noted that we may not use the above method of calculation at very high densities, such that $\omega_p^2 \simeq \omega_o^2$, for then the particle is essentially free but localized to a thin slab.

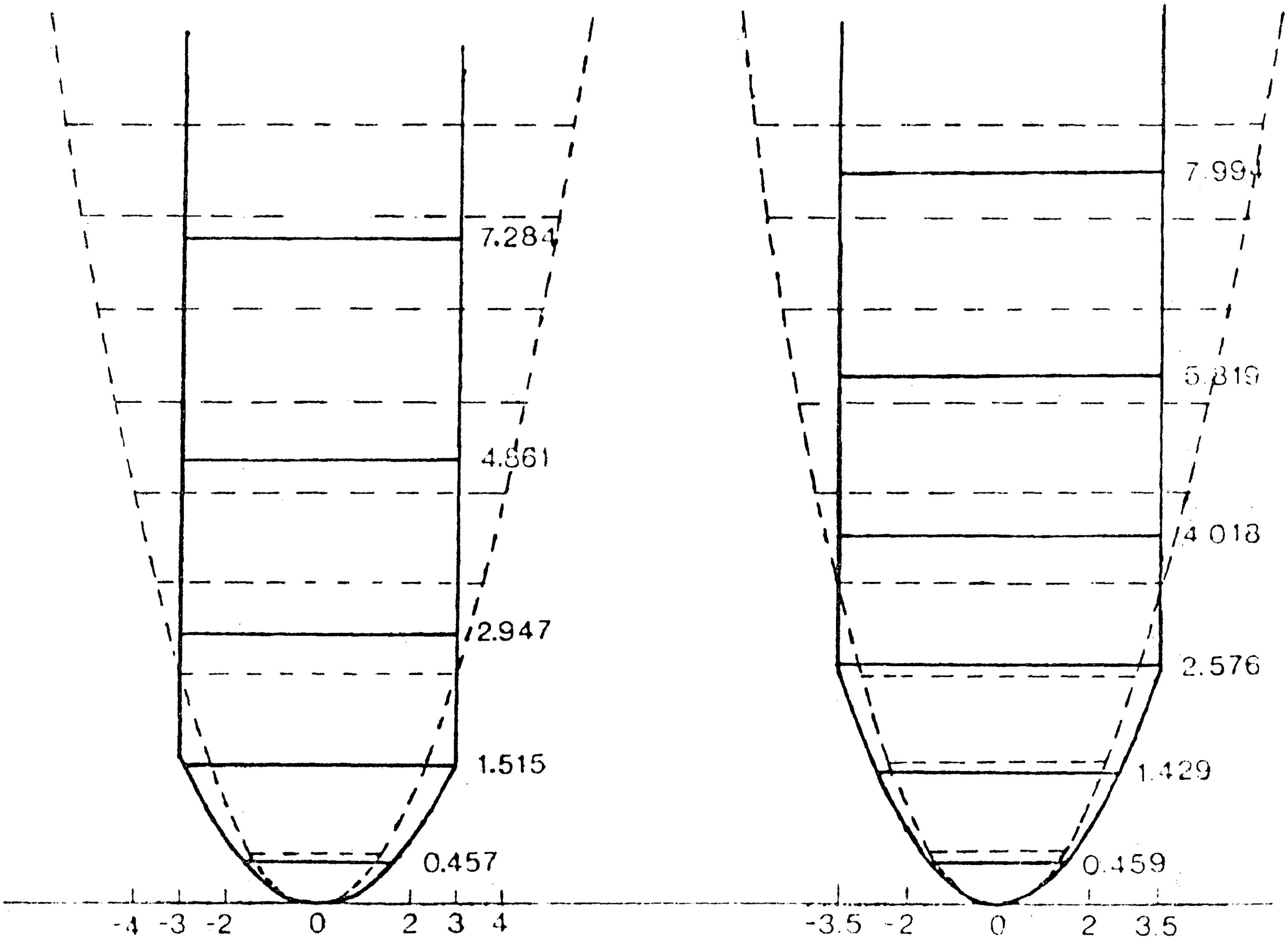


FIG. 16a: Energy levels in the unit of $\hbar\omega_o$ of restricted oscillator with dipolar interaction for $Y_o = 3$ and 3.5 for argon.

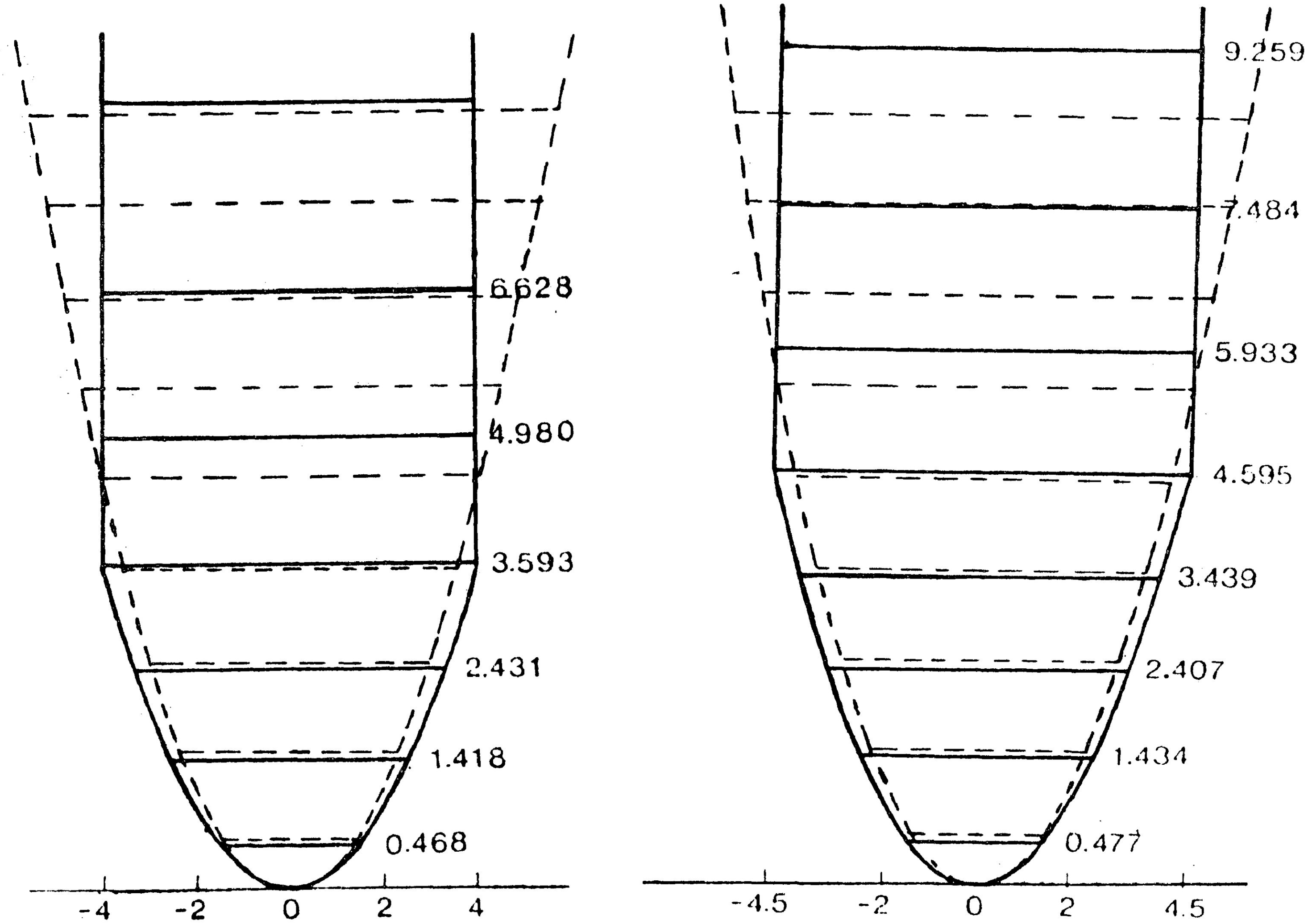


FIG. 16b: Energy levels of restricted oscillator with dipolar interaction for Y_o = 4 and 4.5 for argon.

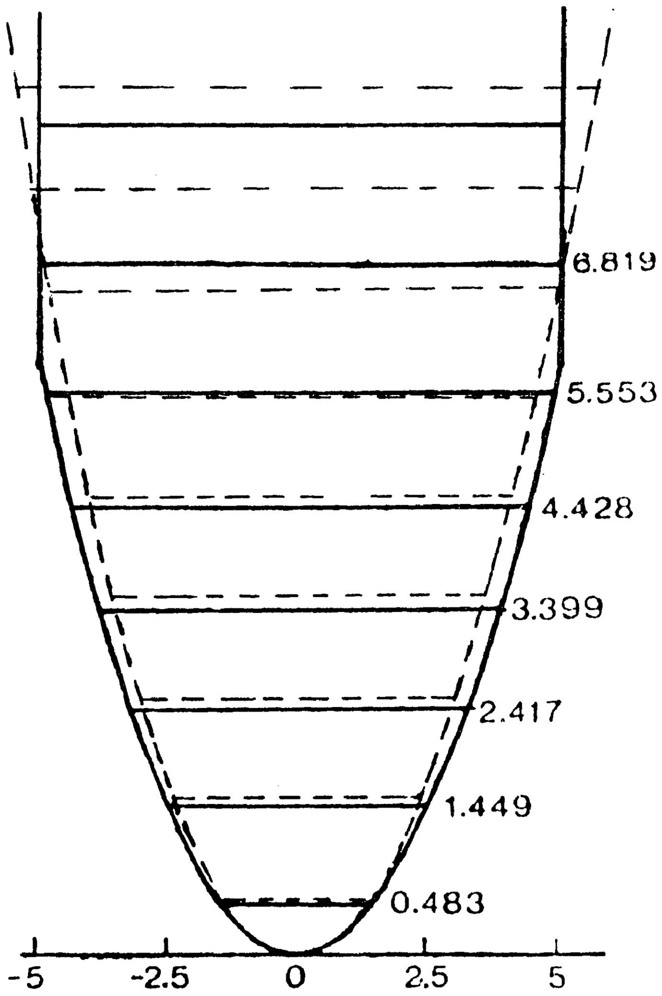


FIG. 16c: Energy levels in the unit of $\hbar\omega_o$ of restricted oscillator with dipolar interaction for $Y_o = 5$ and for argon.

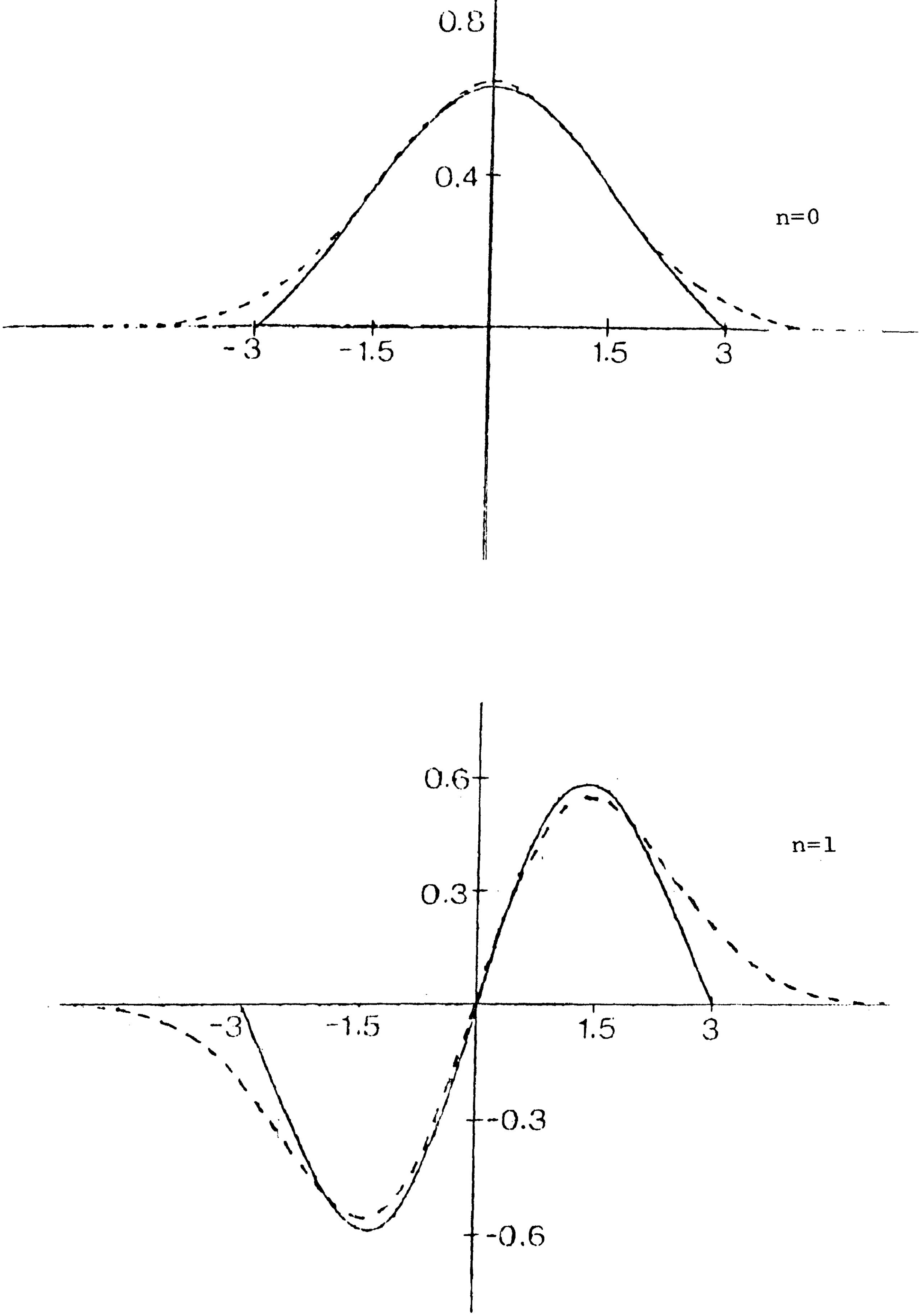


FIG. 17a: Ground state and first excited state of restricted oscillator with dipolar interaction for $Y_o = 3$ and for argon.

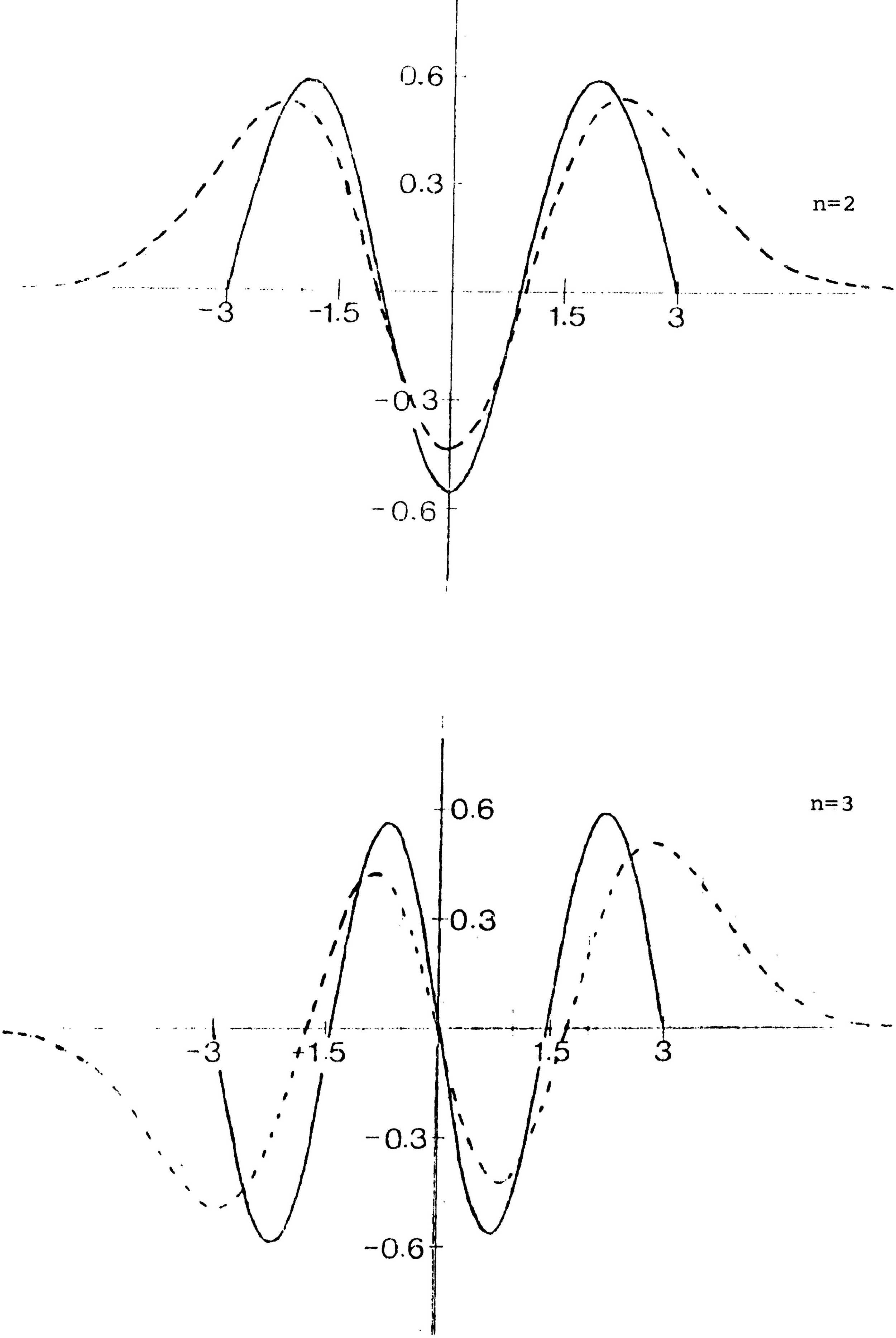


FIG. 17b: Second and third excited states of restricted oscillator with dipolar interaction for $Y_o = 3$ and for argon.

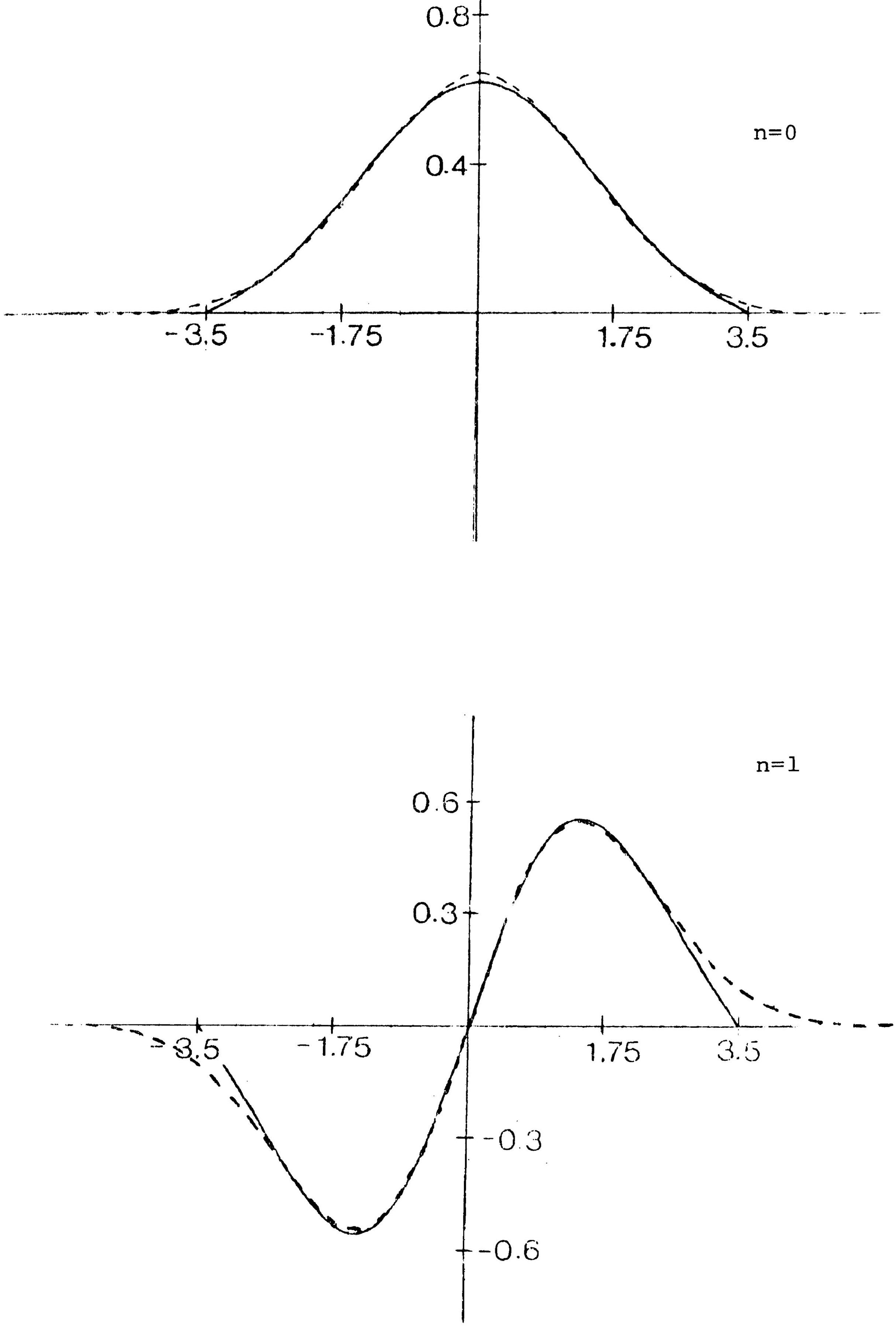


FIG. 18a: Ground state and first excited state wave function of restricted oscillator with dipolar interaction for $Y_o = 3.5$ for argon.

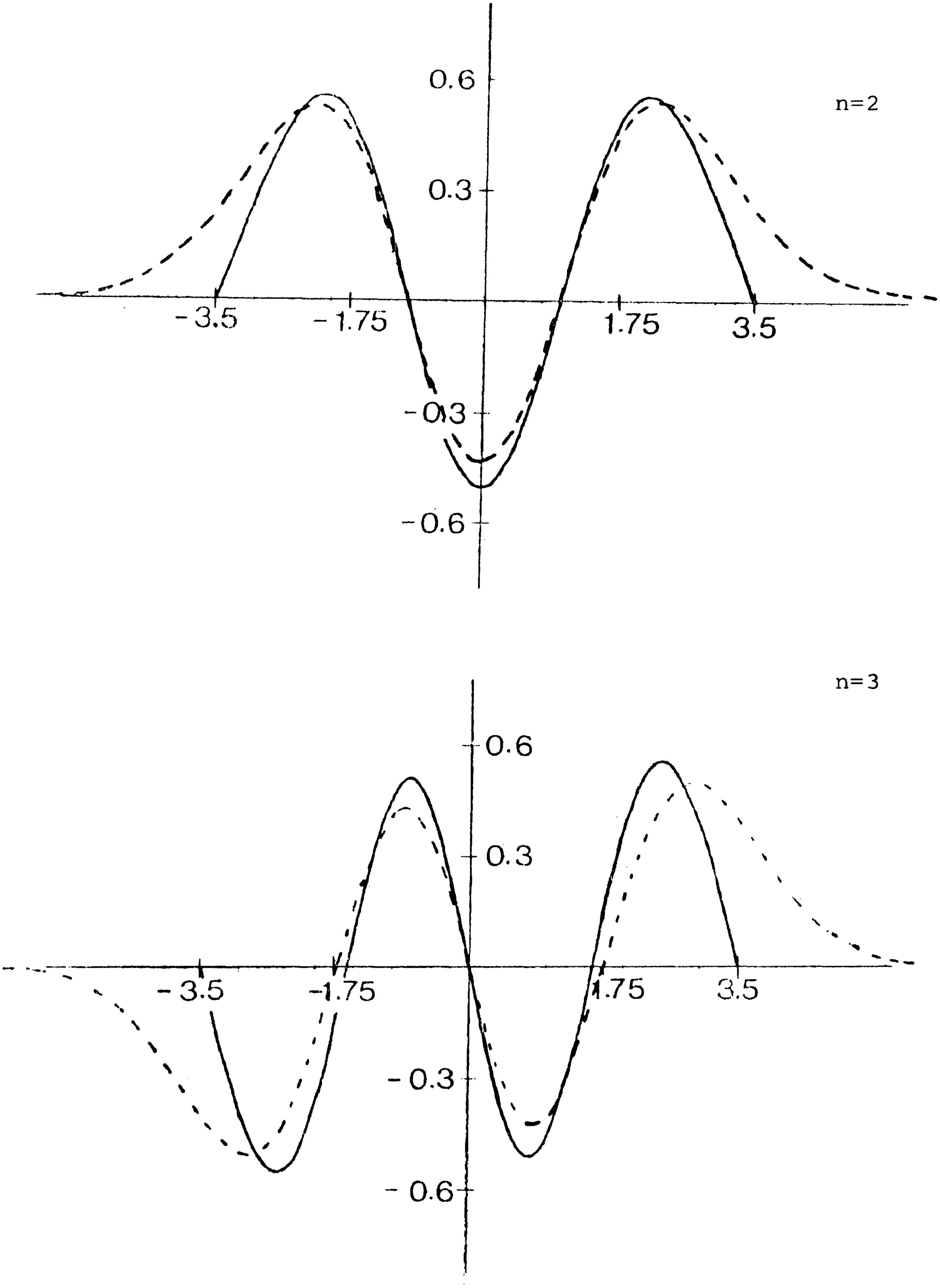


FIG. 18b: Second and third excited state of restricted oscillator with dipolar interaction for $Y_o = 3.5$ for argon.

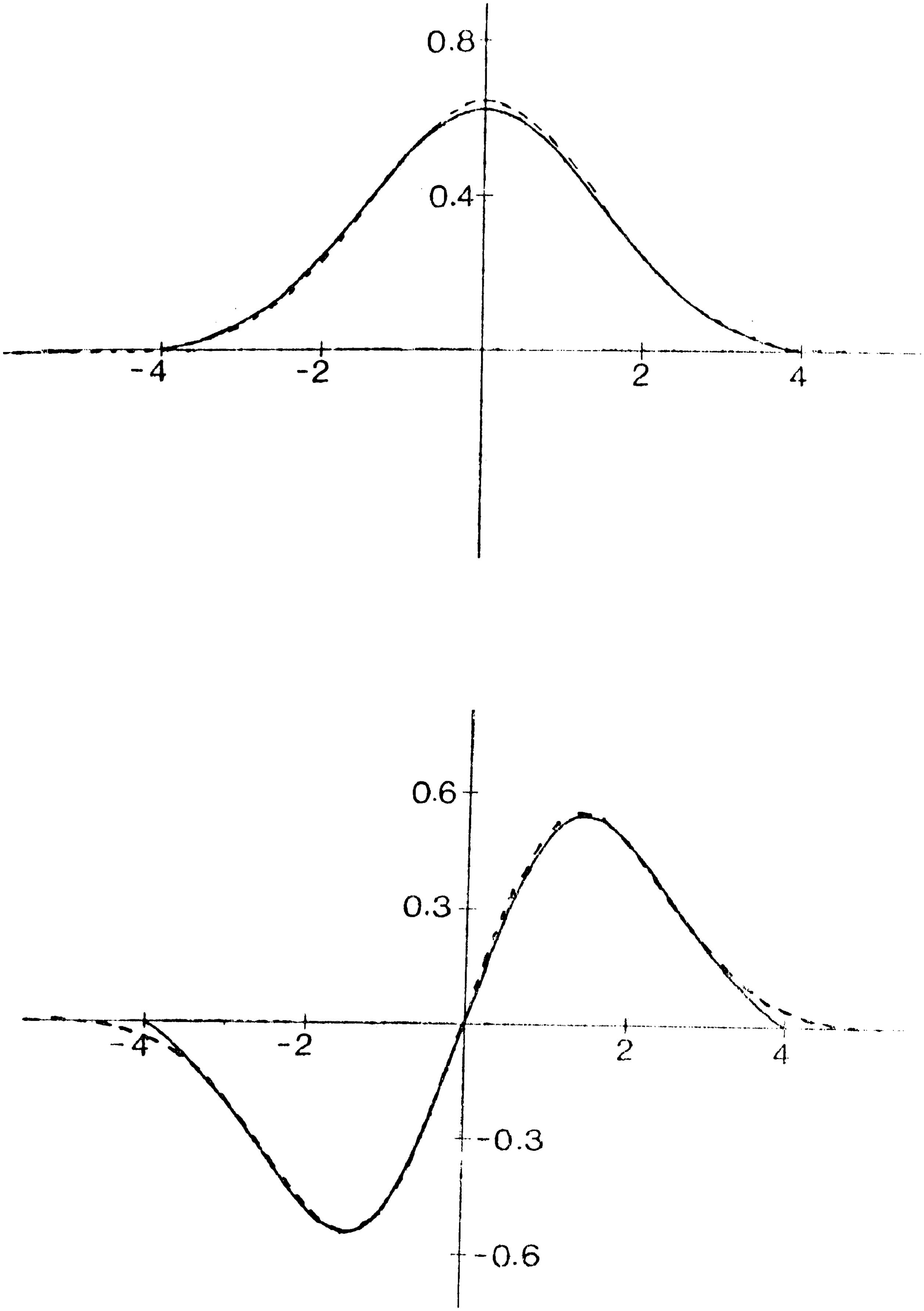


FIG. 19a: Ground state and first excited state wave functions of restricted oscillator with dipolar interaction for $Y_o = 4$ for argon.

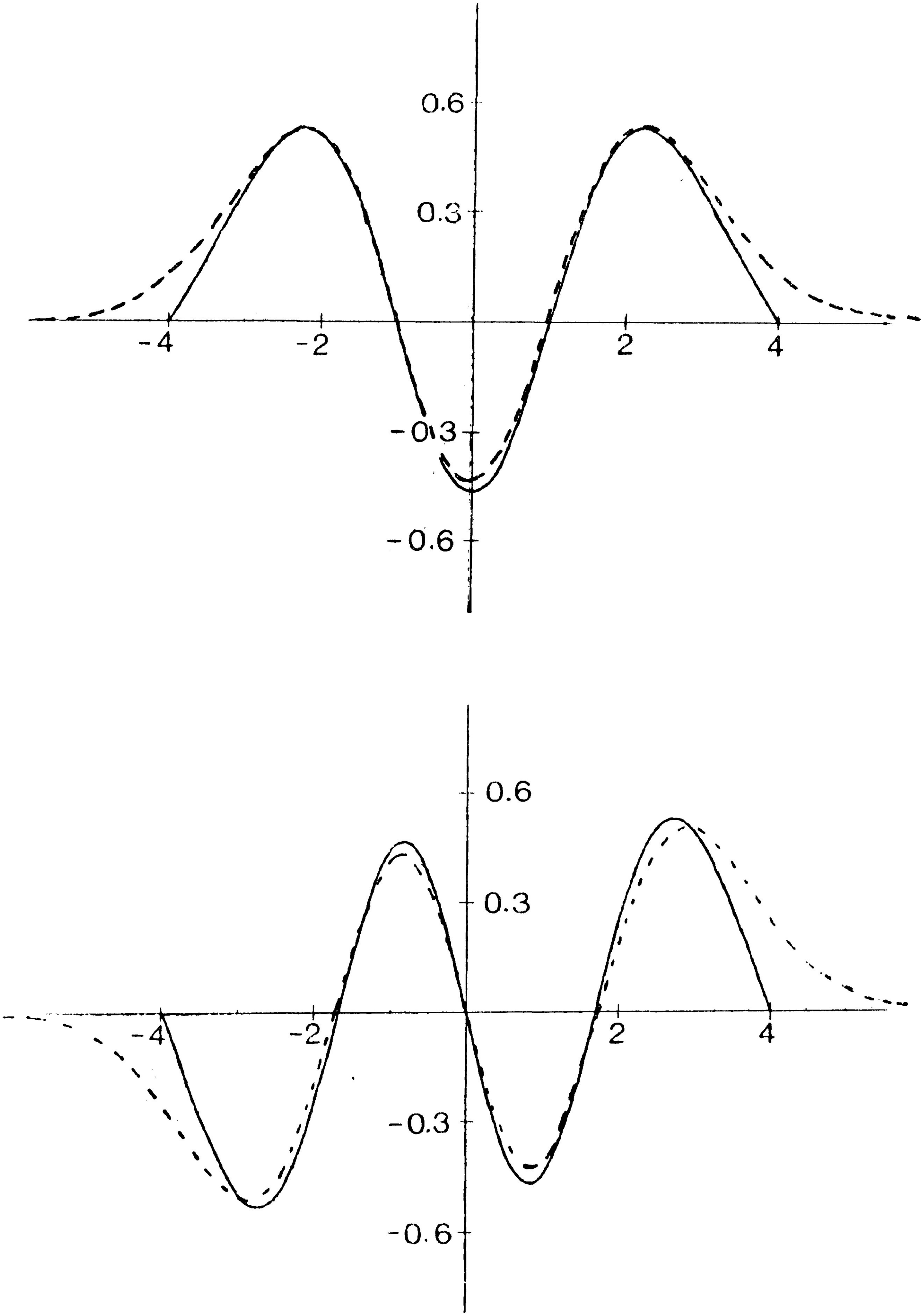


FIG. 19b: Second and third excited state wave functions of restricted oscillator with dipolar interaction for $Y_o = 4$ for argon.

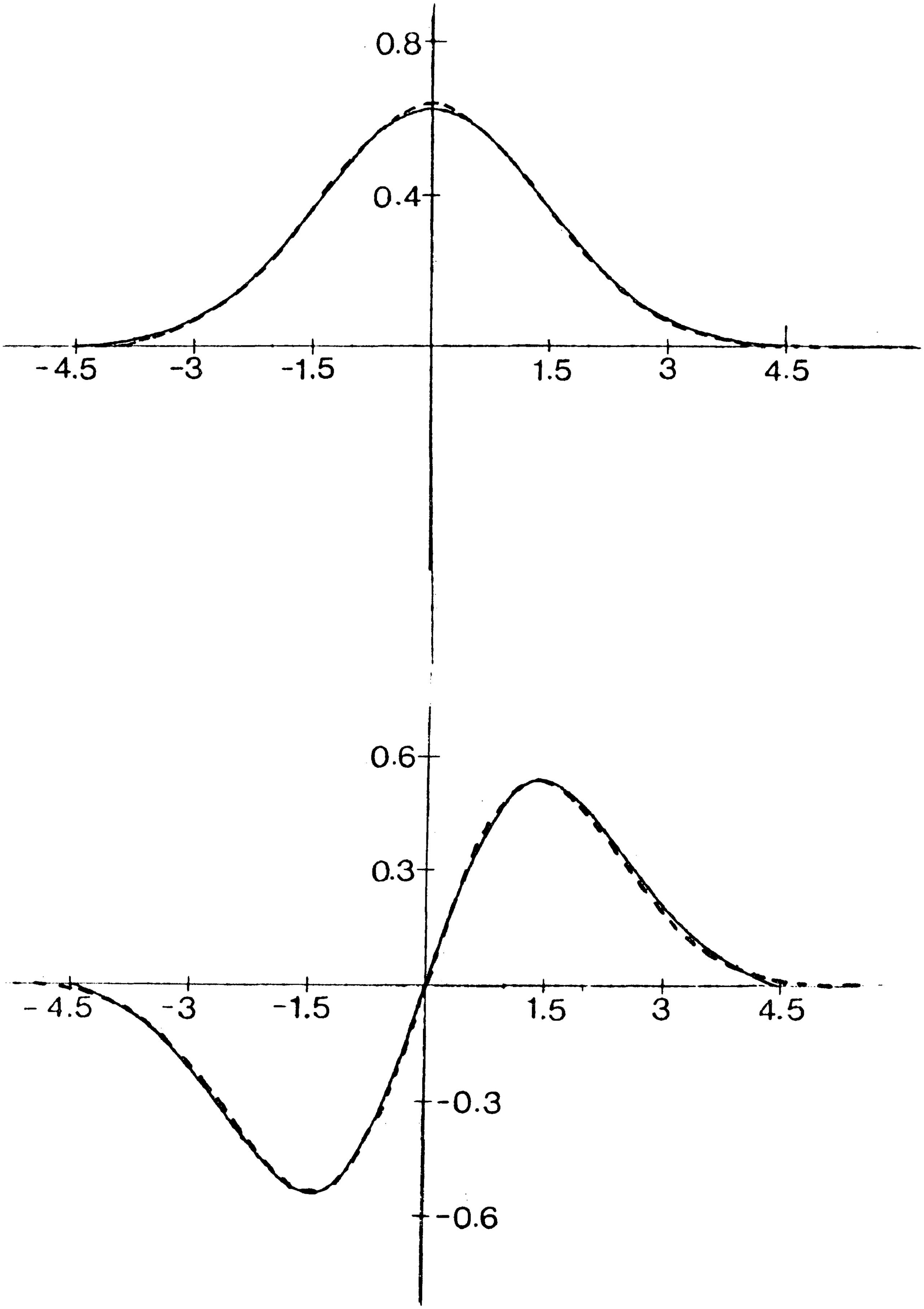
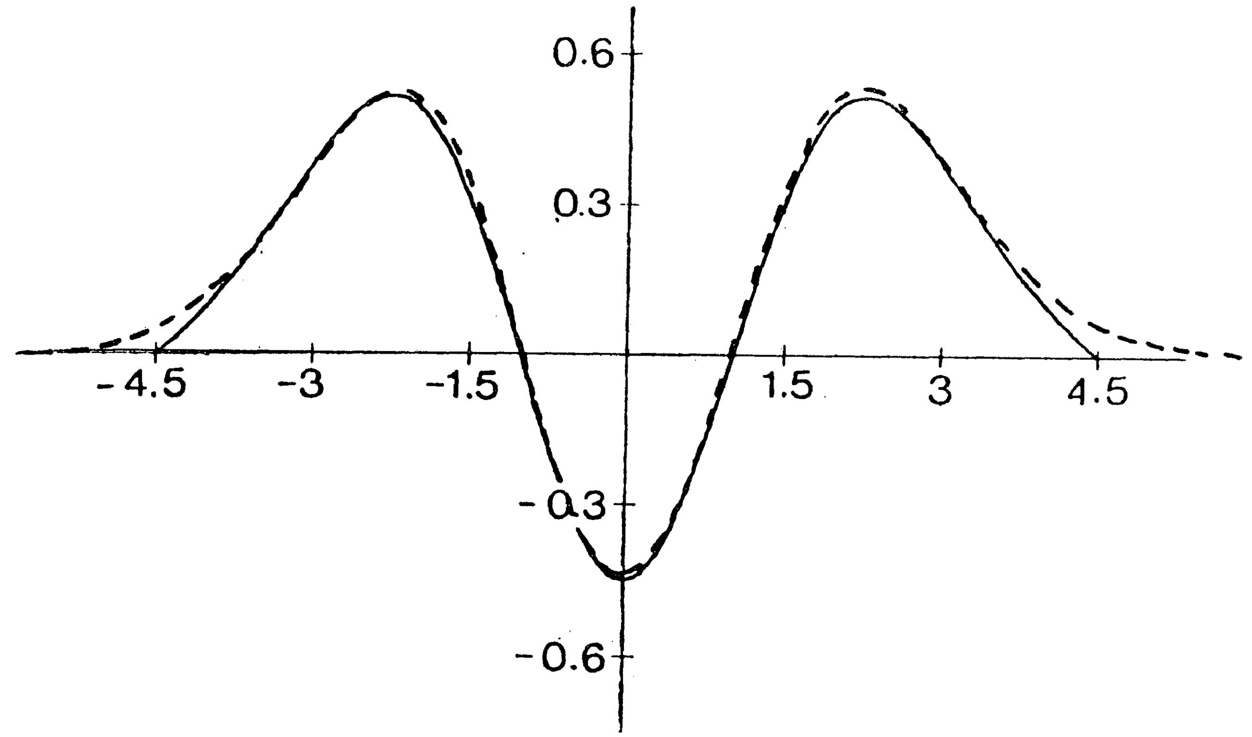


FIG. 19c: Ground state and first excited state wave functions of restricted oscillator with dipolar interaction for $Y_o = 4.5$ for argon.



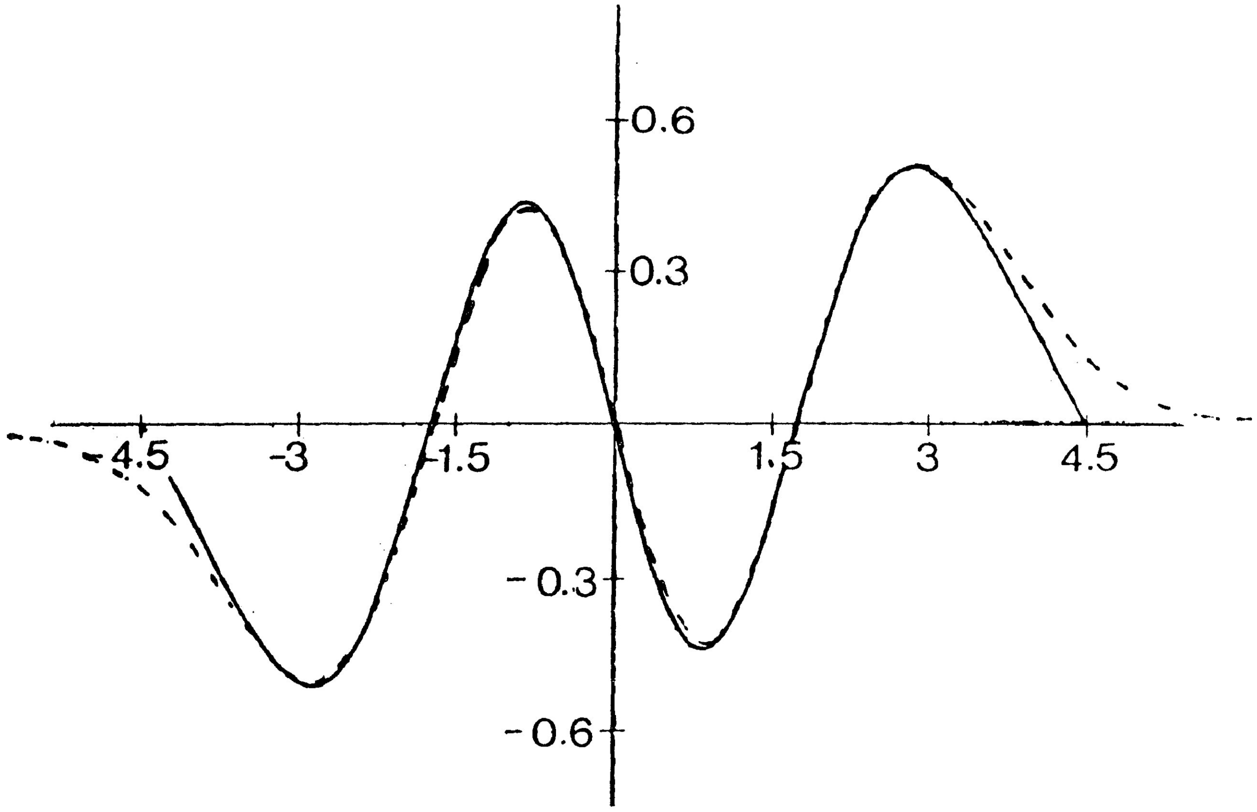


FIG. 20a: Second and third excited state wave functions of restricted oscillator with dipolar interaction for $Y_o = 4.5$ for argon.

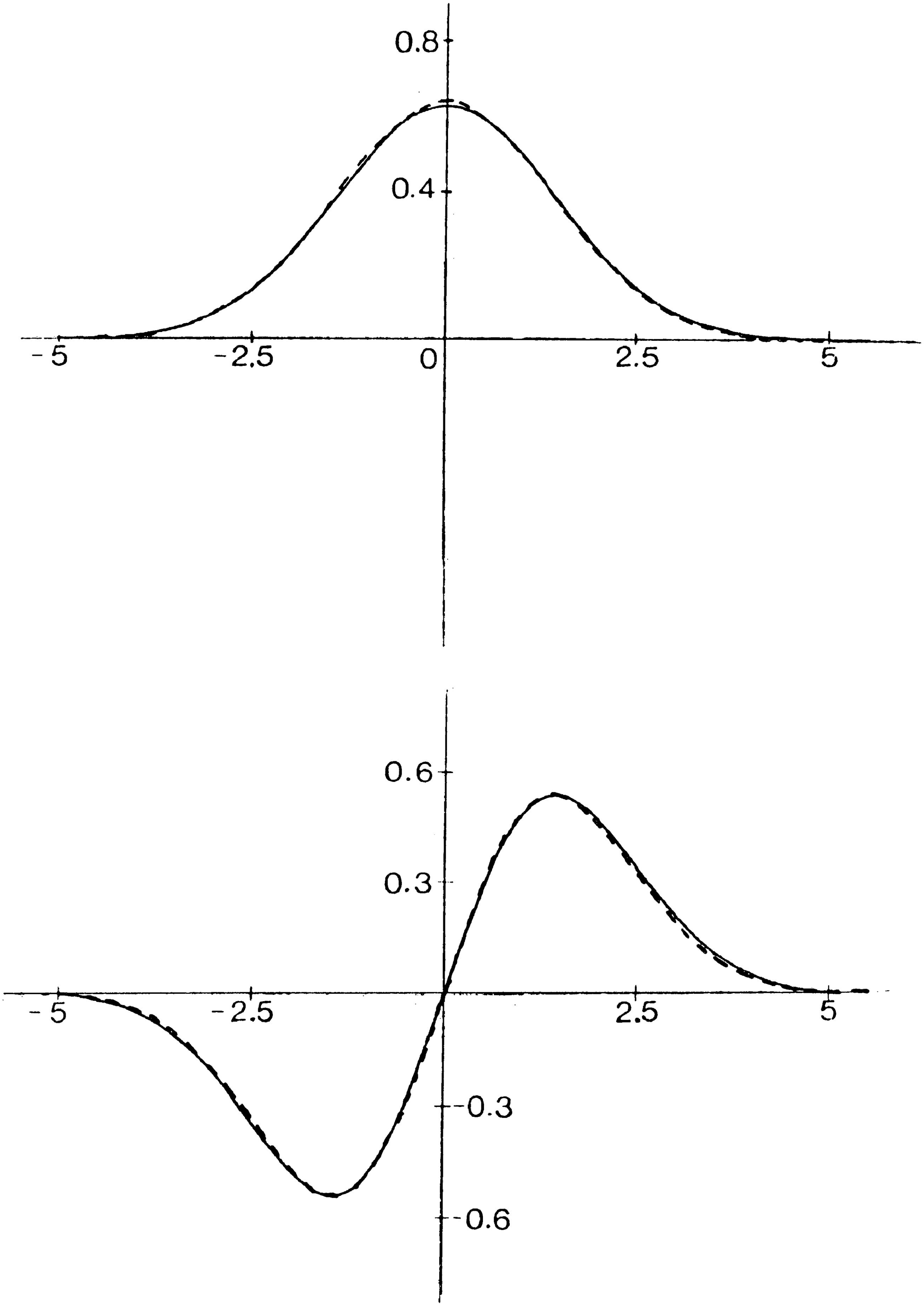


FIG. 20b: Ground state and first excited state wave functions of restricted oscillator with dipolar interaction for $Y_o = 5$ for argon.

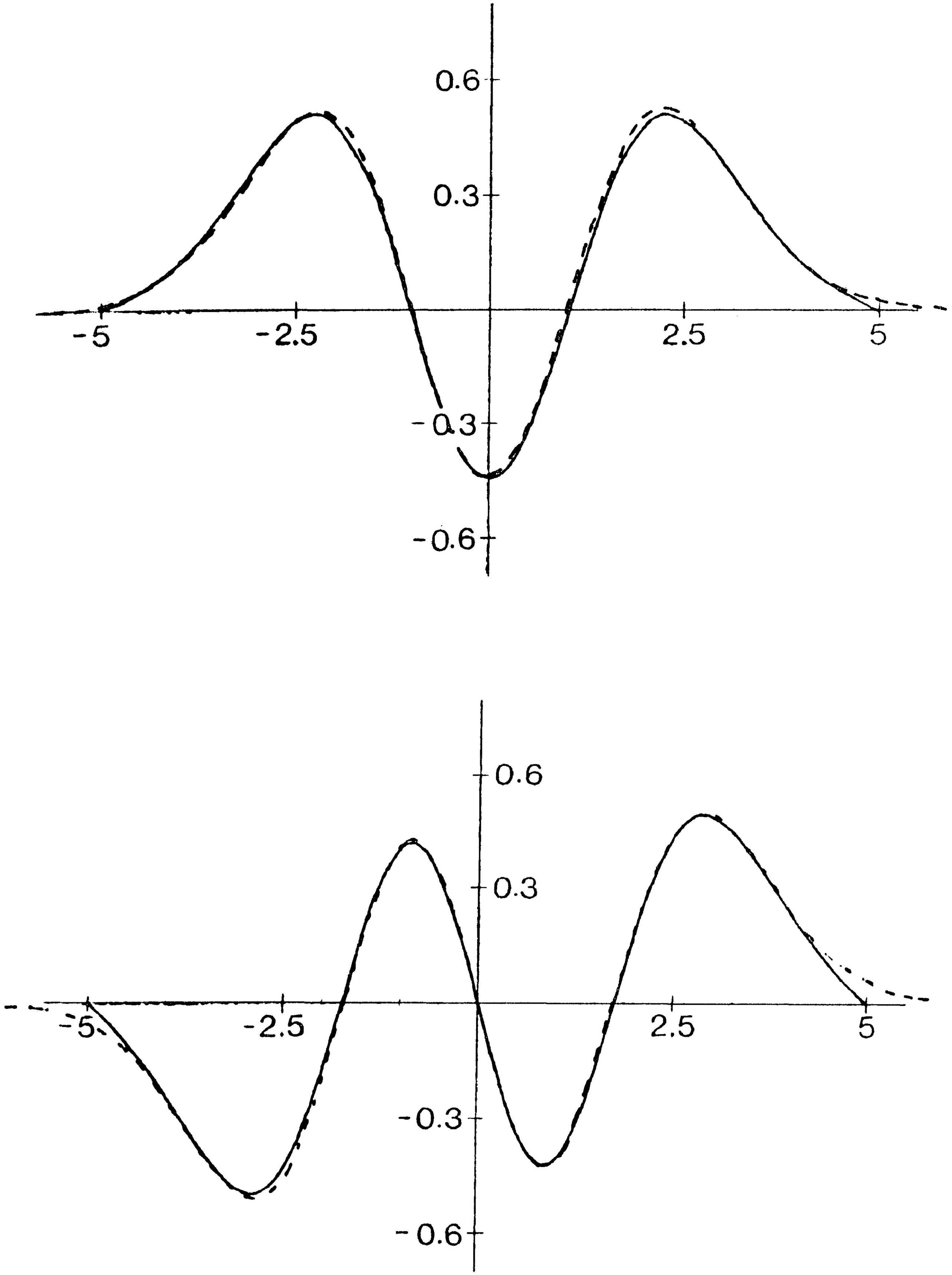


FIG. 20c: Second and third excited state wave function of restricted oscillator with dipolar interaction for $Y_o = 5$ for argon.

We mentioned in Sec. IV that it is difficult to solve exactly the Schrödinger equation given by (III:53). However, we suggested earlier that it might be easier to solve (III:53) by means of perturbation theory assuming that the macroscopic field E is so small that qEx can be treated as a perturbation. According to perturbation theory, the energy of the system is given by:

$$w = w_o + qE\langle\Psi_o|x|\Psi_o\rangle + \sum_{n\neq 0}^{\infty} \frac{|\langle\Psi_n|x|\Psi_o\rangle|^2 q^2E^2}{W_o - W_n} \qquad (V{:}16)$$

where, because of parity, the first order change on the right of (IV:16) vanishes. Thus the ground state polarizability of the restricted oscillator with dipolar interaction is equal to:

$$\alpha \simeq 2q^2 \sum_{n=0}^{\infty} \frac{|\langle\Psi_n(x)|x|\Psi_o(x)\rangle|^2}{W_n - W_o} \qquad (V{:}17)$$

where $\Psi_n(x)$ and W_n are the wave function and the energy of the restricted oscillator with dipolar interaction. Both computed energies and wave functions are dimensionless quantities, and the relationships between dimensional and dimensionless quantities are given by (IV:3) and (IV:29), respectively. Using these in (V:17), the polarizability of the system becomes

$$\alpha = \frac{e^2}{m_e\omega_o^{\,2}} \sum_{n=1}^{\infty} \frac{|\langle\Psi_n(y)|y|\Psi_o(y)\rangle^2}{w_n - w_o} \qquad (V{:}18)$$

The relative polarizability of the restricted simple harmonic oscillator with dipolar interaction is thus:

$$\frac{\alpha}{\alpha_o} = \sum_{n=1}^{\infty} \frac{|\langle\Psi_n(y)|y|\Psi_o(y)\rangle|^2}{w_n - w_o} \qquad \text{(V:19)}$$

where $\alpha_o = e^2/m_e\omega_o^2$ is the polarizability of the isolated molecule. Using the energies and wave functions calculated above, we compute the relative ground state polarizabilities of A, Kr, N_2^* and CO_2 and the results are shown in Fig. 21.

It is to be noted that α/α_o in Fig. 21 shows maxima for the restricted S.H.O. with dipolar interaction. These maxima occur in the range of a few hundred amagats in qualitative agreement with experiment. Here, of course, the one-dimensional C_M function is proportional to α/α_o and given by:

$$C_M = C_M^{(o)}(\alpha/\alpha_o) \qquad \text{(V:20)}$$

where $C_M^o = \frac{4\pi}{3} A\alpha_o$ is the C_M function at zero density.

However, our results for C_M rise more rapidly with increasing density at low densities and fall off more rapidly with increasing density at high densities than do the experimental values. Possible reasons for this will be discussed in Secs. VII and VIII.

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*ω_o for N_2 is found from the C_M function given by Ely and Staty [33].

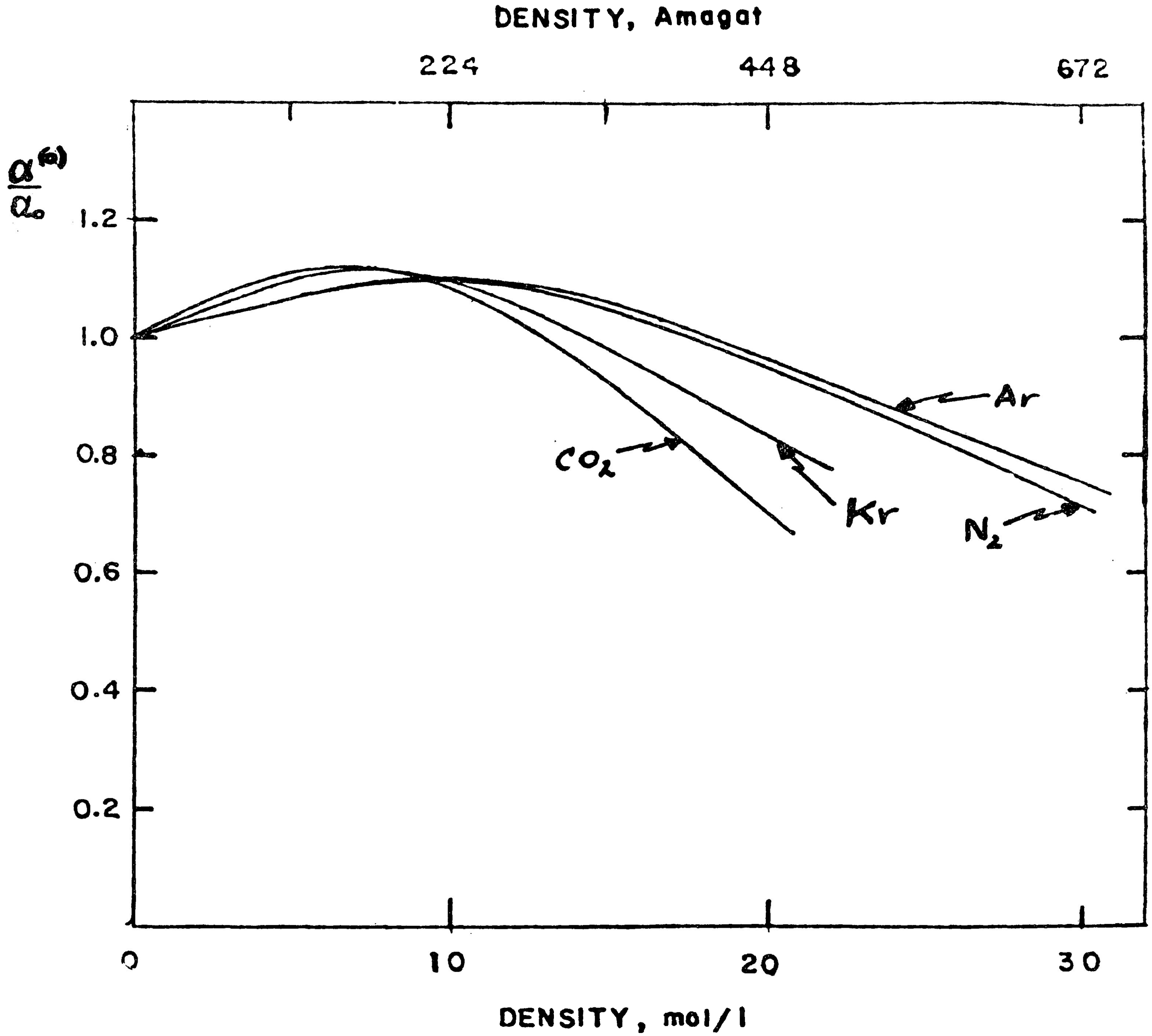

FIG. 21. The ground state polarizability of restricted oscillator with dipolar interaction as a function of density for various gases.

VI. POLARIZABILITIES OF EXCITED STATES AND TEMPERATURE DEPENDENCE OF THE C_M FUNCTION.

In Sections IV and V we derived the ground state polarizability of the restricted, simple harmonic oscillator both with and without dipolar interaction. At T = 0^oK this information is all we require to find the corresponding C_M function, but for T > ^oK some oscillators will be in excited levels and to examine the temperature dependence of the permittivity we should take account of their contribution to the total polarization. Thus in principle both ε and C_M will exhibit temperature as well as density dependence. To discuss the former we first extend the computer calculation to find the polarizabilities of the excited states of the restricted simple harmonic oscillator experiencing dipolar interaction with its neighbours.

If $\alpha_o = e^2/m_o\omega_o{}^2$ is the polarizability of the isolated oscillator, the relative polarizability, $\alpha^{(n)}$ of the n^{th} level is:

$$\alpha^{(n)}/\alpha_o = \sum_{m\neq n} \frac{|<\Psi_m|y|\Psi_n>|^2}{w_m - w_n} \qquad \text{(VI:1)}$$

and in *Appendix B* we calculate (VI:1) directly from knowledge of w_n and ψ_n for the first 8 states. The results for Ar, Kr

CO_2 and N_2 are given in Tables I, II, III and IV, respectively. Plots of $\alpha^{(n)}$ vs. ρ for these gases are also given in Figs. 22, 23, 24 and 25.

It is interesting to note from these results that at sufficiently high densities the polarizabilities of the excited levels can become *negative*, and in this connection it should be recalled that the polarizability of the *isolated* simple harmonic oscillator is the *same* in all states. Now in simple dielectric theory it is usual to associate negative polarizabilities with free or unbounded states of the electron and if we adopt this interpretation here we would conclude that oscillator states n having $\alpha^{(n)} < 0$ do not exist!

Further, consequences of this idea will be discussed in Sec. VIII, but for the present we assume simply that at any given density there are a finite number, N of discrete levels possible where N is the largest quantum number possible for which $\alpha^{(N)} \geq 0$. Clearly N decreases as the density increases.

We also adopt a Clausius-Mossotti approach to the calculation of the permittivity. For $T > 0^{\circ}K$, the medium is now essentially like a mixture of nonpolar, one-dimensional atoms of polarizabilities $\alpha^{(n)}$ and number densities:

$$N^{(n)} = \frac{N_o}{\sigma} e^{-\beta W_n} \qquad \text{(VI:2)}$$

where:

$$\sigma = \sum_{n=0}^{N} e^{-\beta W_n} \qquad \text{(VI:3)}$$

is the partition function of the oscillator with N discrete levels. Here $\beta = (kT)^{-1}$.

Since the local field, $\underset{\sim}{F}$ is still given by (III:32) for all states, the polarization contributed by particles in the level n is:

$$P_n = \alpha^{(n)} N^{(n)} \left[(E+4\pi P)\right] \qquad \text{(VI:5)}$$

Summing (VI:5) over allowed n values and solving for P leads to the dielectric constant:

$$\varepsilon - 1 = \frac{4\pi \sum_{o}^{N} \alpha^{(n)} N^{(n)}}{1 - 4\pi \sum_{o}^{N} \alpha^{(n)} N^{(n)}} \qquad \text{(VI:6)}$$

and (VI:6) gives at once the Clausius-Mossotti function:

$$C_M = \frac{\varepsilon - 1}{3\varepsilon} \left(\frac{W}{\rho}\right) = \frac{4\pi A}{3} <\alpha(T)> \qquad \text{(VI:7)}$$

where, after use of (VI:2), the average polarizability at the temperature T is:

$$\langle\alpha(T)\rangle = \frac{\sum_{o}^{N} \alpha^{(n)} e^{-\beta(W_n - W_o)}}{\sum_{o}^{N} e^{-\beta(W_n - W_o)}} \qquad \text{(VI:8)}$$

Apart from noting that $\langle\alpha\rangle$, and hence C_M, have (vanishingly weak) negative, temperature coefficients, we make no attempt to calculate (IV:8) since clearly in the one-dimensional model the spacing of the energy levels is so great compared to kT that the exponential factors in (IV:8) are negligibly small for all $n \geq 1$. Thus, here, $\langle\alpha\rangle$ reduces essentially to the polarizability, $\alpha^{(o)}$ of the ground state.

In fact, however, we should not use this simple method for estimating effects associated with excited states for although real atoms in any state of excitation can be looked upon as oscillators, the fundamental frequencies associated with their excited levels decrease as the quantum numbers of the levels increase.* Thus the extreme *concavity* of the restricted harmonic oscillator potential compared with the *convexity* of the potential in real atoms precludes use of

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*For example, in hydrogen, the polarizability of the n^th level is $\alpha^{(n)} = (n+1)^6 \alpha^{(o)}$ (large $n \geq 0$) where $\alpha^{(o)} \equiv e^2/m_o\omega_o^2$ is the ground state polarizability. Letting $\alpha^{(n)} \equiv e^2/m_o\omega_n^2$, the fundamental frequency ω_n of the n^th level compared to that of the ground state is seen to be:

$$\omega_n = \omega_o/(n+1)^3 \qquad \text{(VI:9)}$$

the former to predict any significant results associated with the excited states of real atoms. For this reason we cannot estimate the oscillatory contribution to the specific heat of the gas. However, it is possible to compute a density-dependent contribution to the equation of state arising from the internal, oscillatory motions in the atoms. At $T = 0^{\circ}K$ the latter contribution arises purely from the density-dependence of the ground state energy of the restricted harmonic oscillator, either with or without dipolar interaction with its neighbours. Of course, for the isolated atom this contribution to the pressure is entirely absent.

TABLE 1

ARGON

DENSITY		HIGHER STATE POLARIZABILITIES			
Amagat	mol/l	$\frac{\alpha^{(0)}}{\alpha_0}$	$\frac{\alpha^{(1)}}{\alpha_0}$	$\frac{\alpha^{(2)}}{\alpha_0}$	$\frac{\alpha^{(3)}}{\alpha_0}$
67.7	3.024	1.03897	1.03878	1.03646	1.01955
117.0	5.225	1.06833	1.05290	0.95243	0.63241
132.2	5.906	1.07677	1.04518	0.87578	0.45321
150.2	6.710	1.08571	1.02493	0.75835	0.24869
160.5	7.167	1.09018	1.00743	0.67976	0.13619
171.7	7.667	1.09427	0.98472	0.60237	0.05773
197.4	8.816	1.10077	0.91659	0.41965	-0.09274
228.5	10.205	1.10240	0.81478	0.23217	-0.18909
266.5	11.903	1.09485	0.67934	0.06529	-0.23303
313.5	13.999	1.07307	0.53858	-0.06125	-0.23671
341.1	15.234	1.05502	0.43178	-0.10955	-0.23115
372.1	16.618	1.03164	0.34963	-0.13942	-0.21549
446.3	19.932	0.96662	0.18934	-0.17311	-0.18262
541.7	24.190	0.87714	0.05827	-0.17368	-0.14711
666.2	29.753	0.76653	-0.03426	-0.15438	-0.11400

TABLE 2

KRYPTON

DENSITY		HIGHER STATE POLARIZABILITIES			
Amagat	mol/l	$\frac{\alpha^{(0)}}{\alpha_0}$	$\frac{\alpha^{(1)}}{\alpha_0}$	$\frac{\alpha^{(2)}}{\alpha_0}$	$\frac{\alpha^{(3)}}{\alpha_0}$
49.5	2.212	1.04343	1.04084	1.04084	1.02344
64.3	2.872	1.05704	1.05495	1.03557	0.93621
85.6	3.823	1.07650	1.06040	0.95652	0.62897
96.8	4.321	1.08614	1.05308	0.87520	0.43470
109.9	4.910	1.09647	1.03272	0.75358	0.22646
125.6	5.610	1.10664	0.99154	0.59280	0.03492
144.4	6.450	1.11486	0.92168	0.40808	-0.10941
167.2	7.467	1.11825	0.81672	0.21786	-0.20273
195.0	8.709	1.11242	0.67711	0.05165	-0.24317
229.4	10.243	1.09191	0.51181	-0.07529	-0.24371
272.2	12.159	1.05121	0.33960	-0.14830	-0.21777
326.6	14.584	0.98592	0.17739	-0.17984	-0.18379
396.3	17.700	0.89517	0.04495	-0.17830	-0.14767

TABLE 3

NITROGEN

DENSITY		HIGHER STATE POLARIZABILITIES			
Amagat	mol/l	$\frac{\alpha^{(0)}}{\alpha_0}$	$\frac{\alpha^{(1)}}{\alpha_0}$	$\frac{\alpha^{(2)}}{\alpha_0}$	$\frac{\alpha^{(3)}}{\alpha_0}$
64.7	2.891	1.03958	1.03939	1.03706	1.02009
84.0	3.753	1.05191	1.04999	1.03107	0.93405
111.9	4.996	1.06947	1.05392	0.95300	0.63195
143.7	6.416	1.08722	1.02578	0.75404	0.23407
164.2	7.331	1.09601	0.98515	0.59623	0.04336
188.7	8.429	1.10272	0.91669	0.41441	-0.10143
254.8	11.381	1.09724	0.67782	0.05965	-0.23837
299.7	13.385	1.07557	0.51622	-0.06622	-0.24057
355.8	15.889	1.03429	0.34743	-0.14064	-0.21579
426.7	19.057	0.96924	0.18774	-0.17404	-0.18278
517.9	23.129	0.87958	0.05648	-0.17432	-0.14719

TABLE 4

CARBON DIOXIDE

DENSITY		HIGHER STATE POLARIZABILITIES			
Amagat	mol/l	$\frac{\alpha^{(0)}}{\alpha_0}$	$\frac{\alpha^{(1)}}{\alpha_0}$	$\frac{\alpha^{(2)}}{\alpha_0}$	$\frac{\alpha^{(3)}}{\alpha_0}$
43.4	1.940	1.04547	1.04526	1.04282	1.02597
56.4	2.528	1.05975	1.05759	1.03822	0.94169
75.0	3.352	1.08022	1.06381	0.96011	0.63776
96.4	4.304	1.10135	1.03667	0.75772	0.23602
126.6	5.655	1.12130	0.92502	0.40902	-0.10619
146.6	6.546	1.12555	0.81914	0.21778	-0.20020
238.7	10.659	1.06028	0.33530	-0.15235	-0.21864
347.4	15.516	0.90355	0.03869	-0.18038	-0.14791

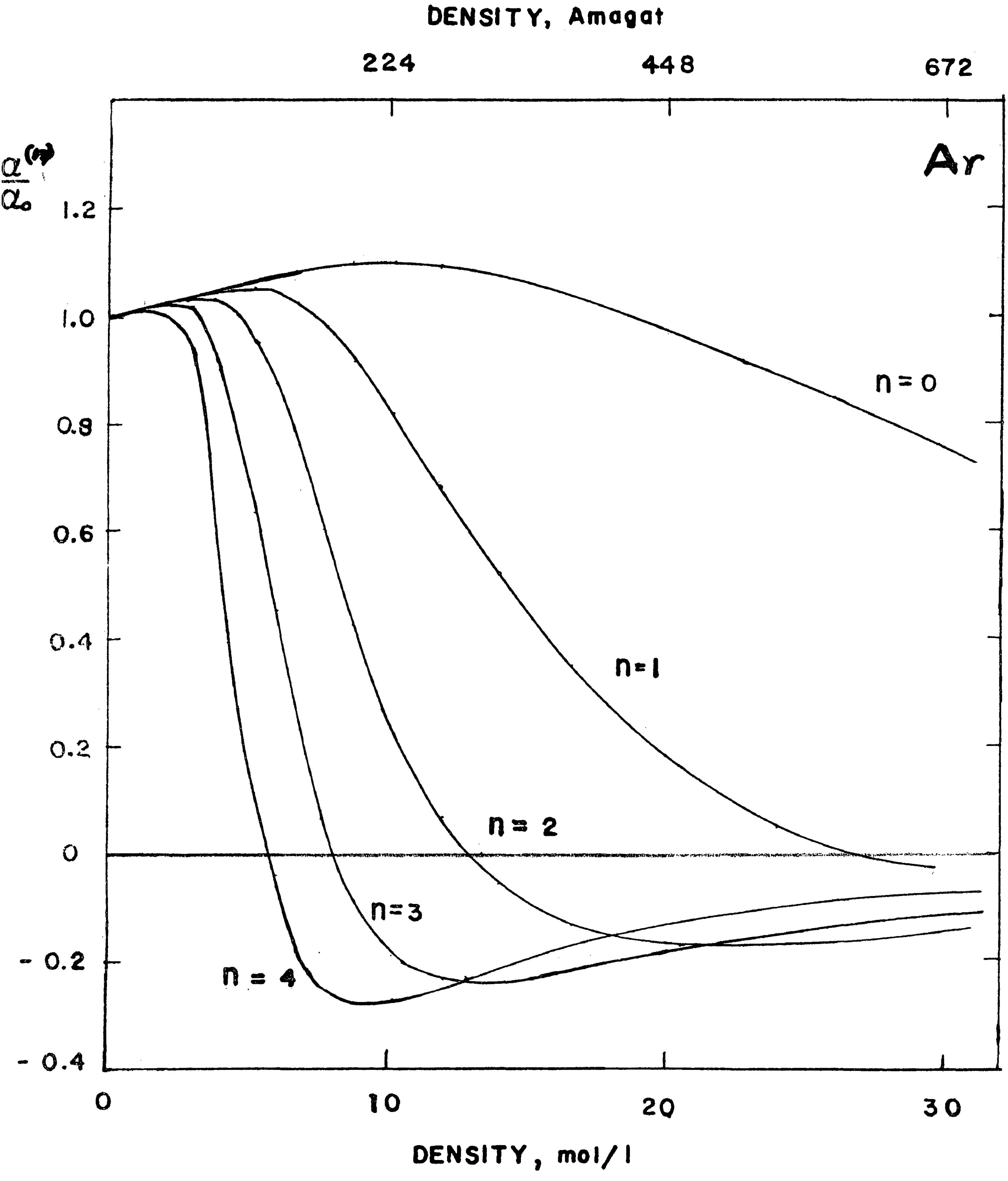

FIG. 22. Polarizabilities of excited states of restricted oscillator with dipolar interaction for Argon.

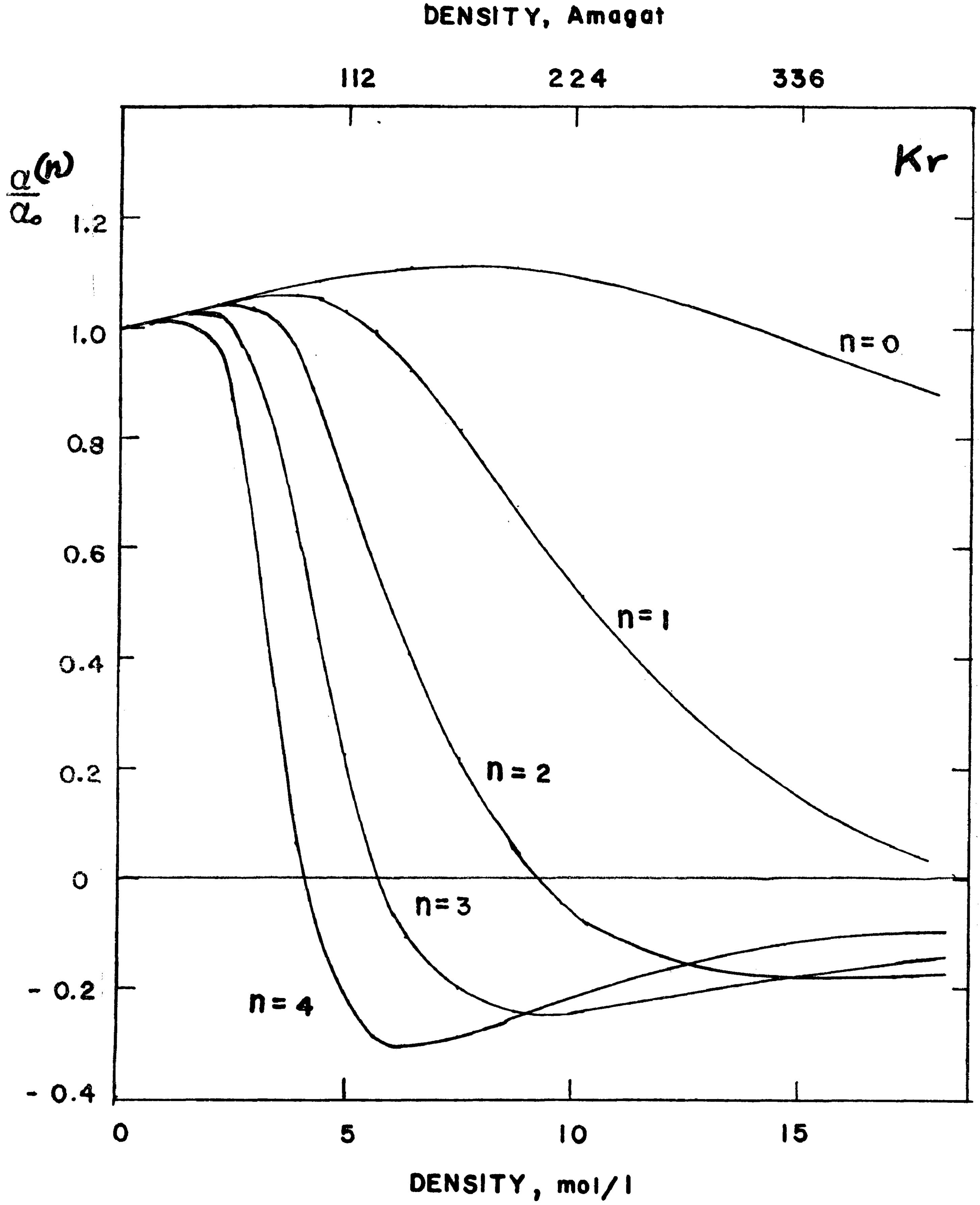

FIG. 23. Polarizabilities of excited states of restricted oscillator with dipolar interaction for Krypton.

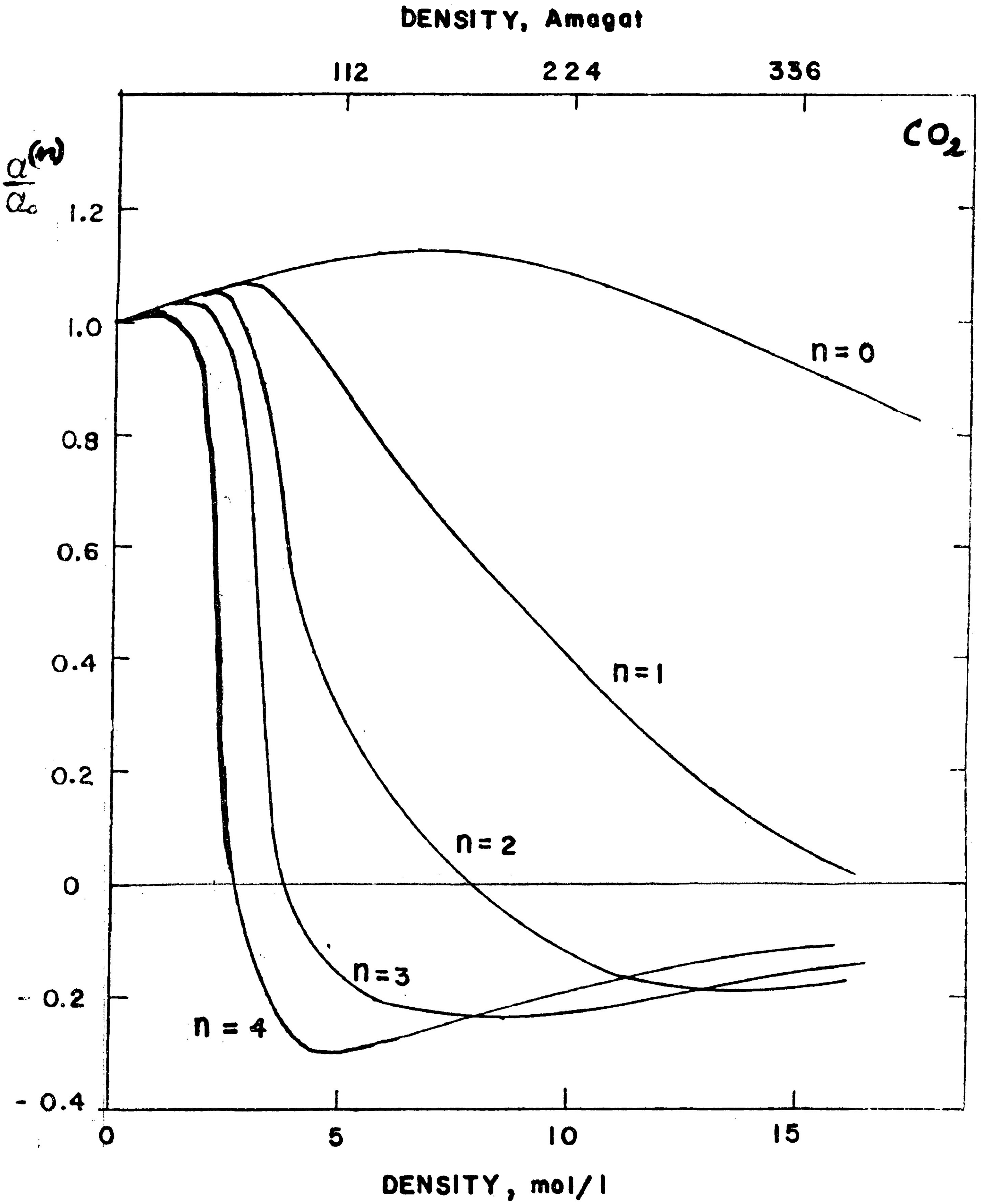

FIG. 24. Polarizabilities of excited states of restricted oscillator with dipolar interaction for CO_2.

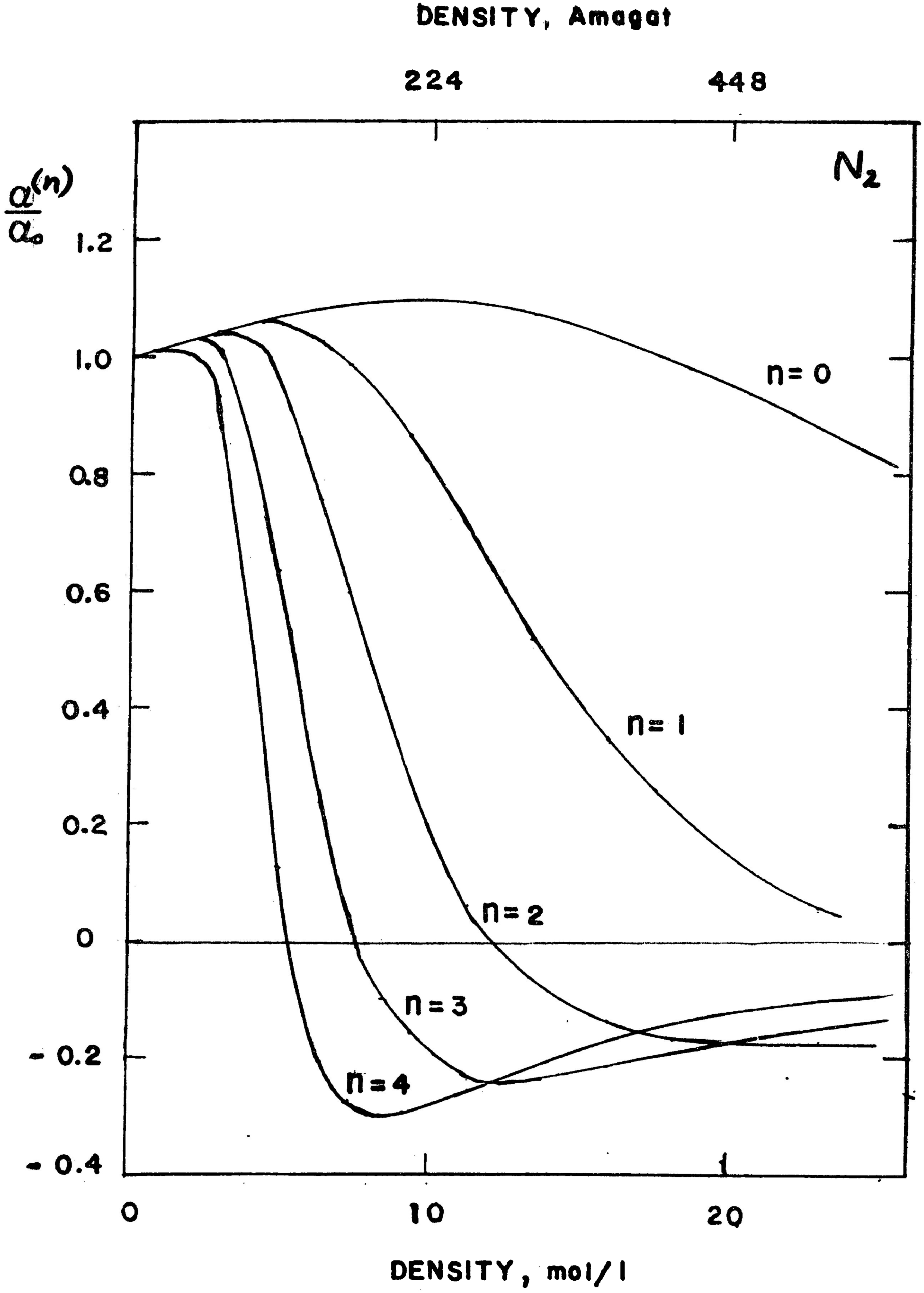

FIG. 25. Polarizabilities of excited states of restricted oscillator with dipolar interaction for Nitrogen.

VII. RESULTS

There are two ways of comparing the present theory with experiment.

(a) Comparison of Permittivities

In the first, we recognize that ε_s refers to a common property in both the one-dimensional theory developed here and the three-dimensional experimental results. However, as seen by (III:31) and (III:47), the Clausius-Mossotti formulae differ for the two cases. If we now replace α_o in (III:31) and (III:47) by $\alpha = \alpha_o(\alpha/\alpha_o)$, the three-dimensional and one-dimensional C_M functions (herein called $C_M^{(3)}$ and $C_M^{(1)}$, respectively) become:

$$C_M^{(3)} = \frac{\varepsilon_s - 1}{\varepsilon_s + 2}\left(\frac{W}{\rho}\right) = \frac{4\pi A\alpha_o}{3}\left(\frac{\alpha}{\alpha_o}\right) \tag{VII:1}$$

$$C_M^{(1)} = \frac{\varepsilon_s - 1}{3\varepsilon_s}\left(\frac{W}{\rho}\right) = \frac{4\pi A\alpha_o}{3}\left(\frac{\alpha}{\alpha_o}\right) \tag{VII:2}$$

and from (VII:1) and (VII:2) the experimental and theoretical static dielectric constants are:

<u>Expt.</u>: $$\varepsilon_s = \frac{1+2\left(\frac{\rho}{W}\right)C_M^{(3)}}{1-2\left(\frac{\rho}{W}\right)C_M^{(3)}} \tag{VII:3}$$

<u>Theory</u>: $$\varepsilon_s = \frac{1}{1-3\left(\frac{\rho}{W}\right)C_M^{(1)}} \tag{VII:4}$$

Next, using experimental results for $C_M^{(3)}$ and the calculated values of $C_M^{(1)}$, found using (V:19) and (V:20), we may plot ε_s vs. ρ for both cases. The results for A, Kr, CO_2 and N_2 are shown in Figs. 26, 27, 28 and 29, respectively.

It may be noted that over most of the density range the theoretical results are slightly higher than the experimental ones by as much as 4%∽5% in the mid-range of densities, but lower than the experimental values at high densities.

These results may be considered reasonably satisfactory, but they are, in fact, quite misleading in that we should really be comparing $C_M^{(3)}$ from experiment with $C_M^{(1)}$ from theory.

(b) Comparison of C_M Functions

When this step is taken the results are far from satisfactory as indicated by Figs. 30 and 31 which compare the experimental ($C_M^{(3)}$) and theoretical ($C_M^{(1)}$) Clausius-Mossotti functions for argon and krypton, respectively. Similarly unsatisfactory results hold for other gases examined.

In all cases the theoretical $C_M^{(1)}$ function achieves a maximum at roughly the same density as found for $C_M^{(3)}$

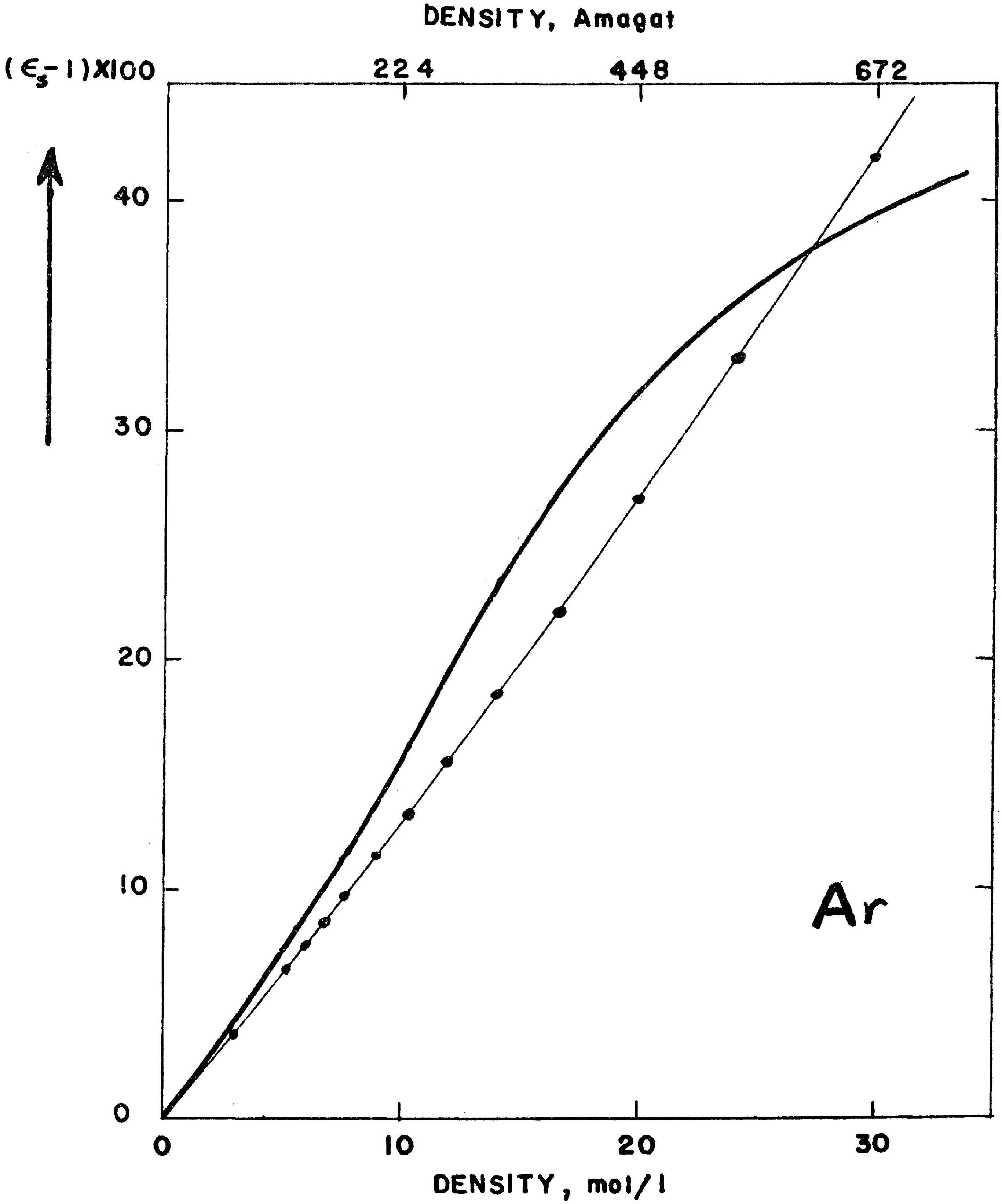

FIG. 26. Static Permittivity of Argon vs. density.

━━━━ Present theory

—•—•—•— Experiment (Ref. [5])

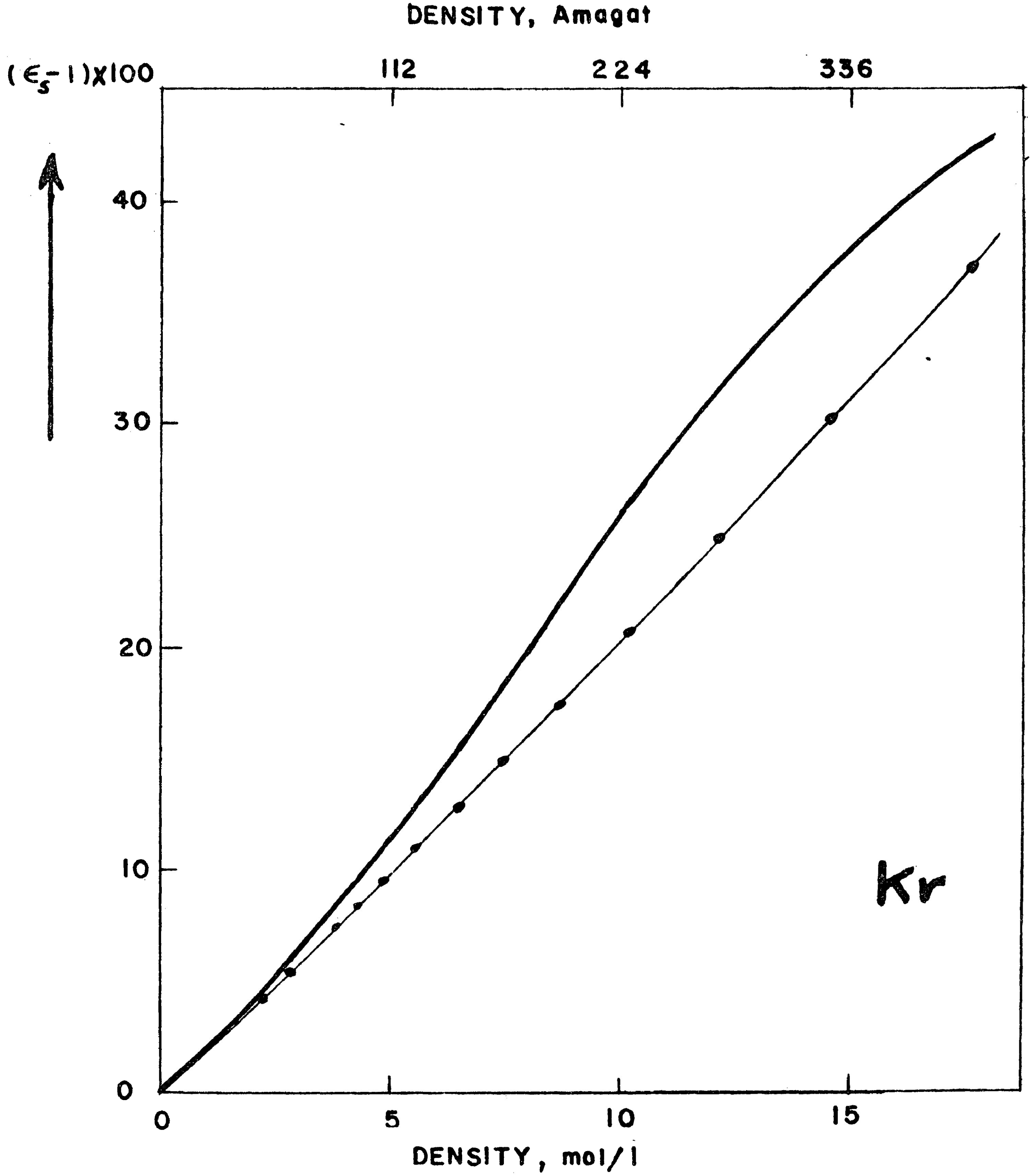

FIG. 27. Static permittivity of Krypton vs. density.

——— Present theory

-•-•-•- Experiment (Ref. [10])

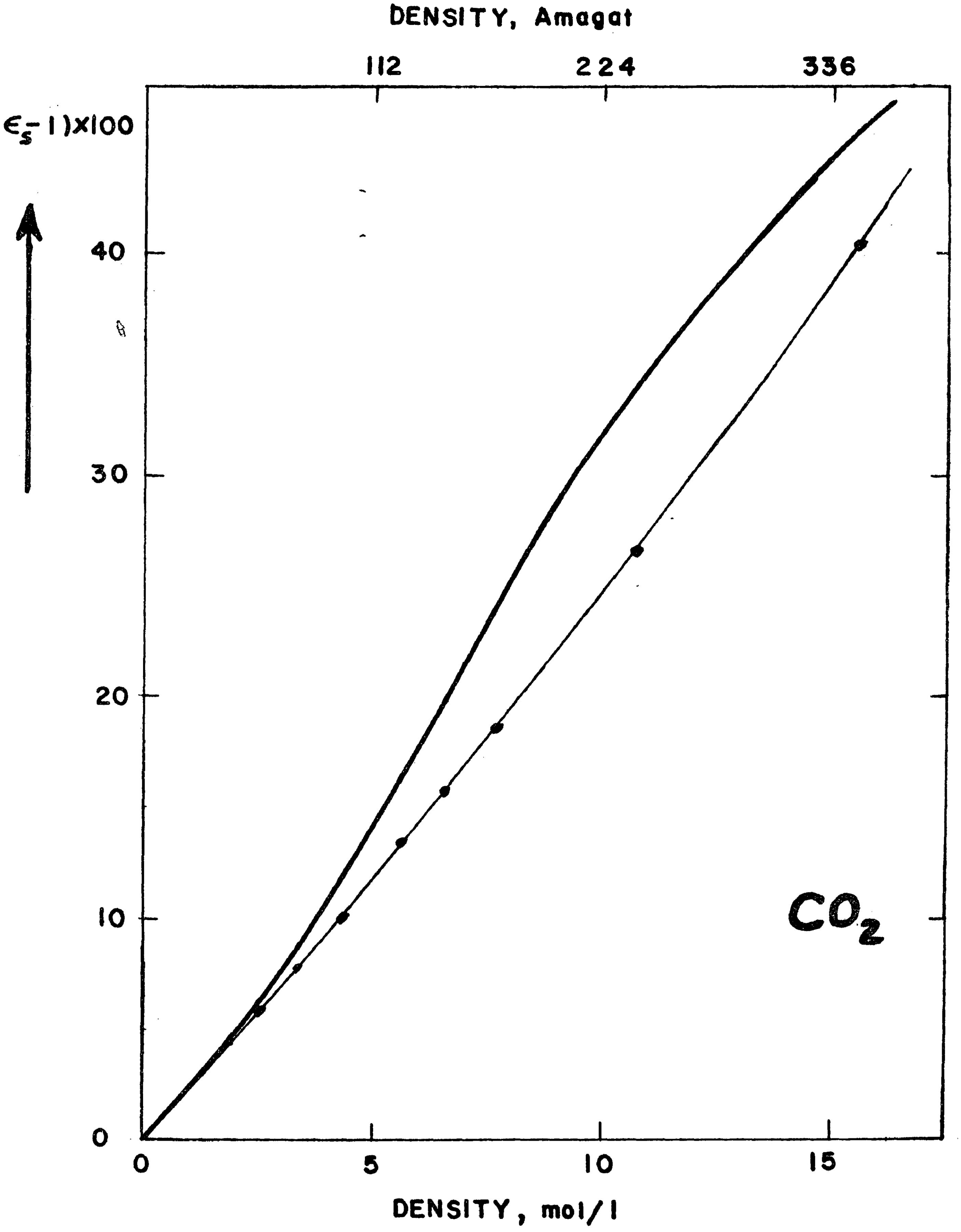

FIG. 28. Static permittivity of Carbon Dioxide vs. density.

━━━━ Present theory

—•—•—•— Experiment (Ref. [4])

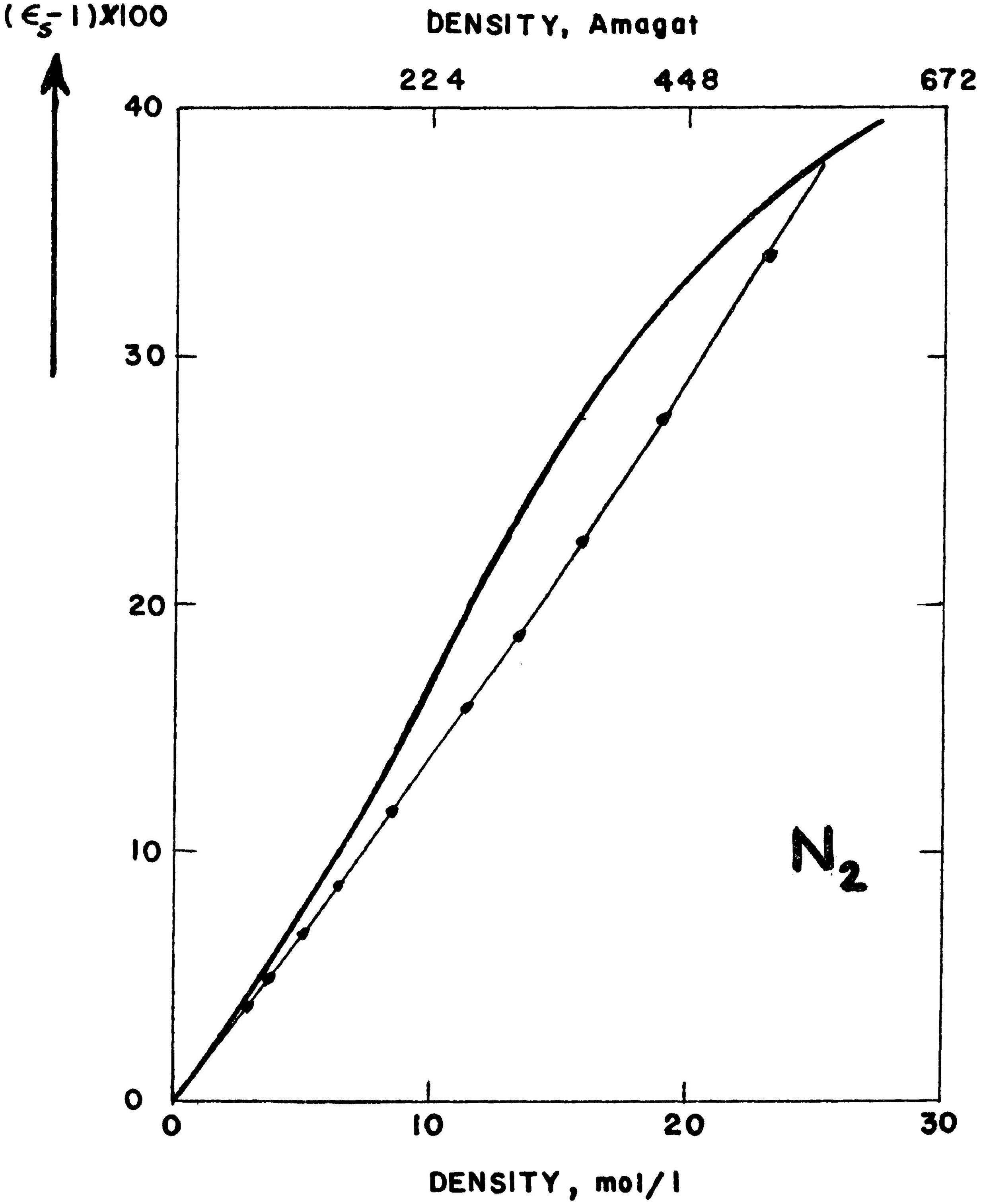

FIG. 29. Static permittivity of Nitrogen vs. density.

▬▬ Present theory

•—•—•—• Experiment (Ref. [33])

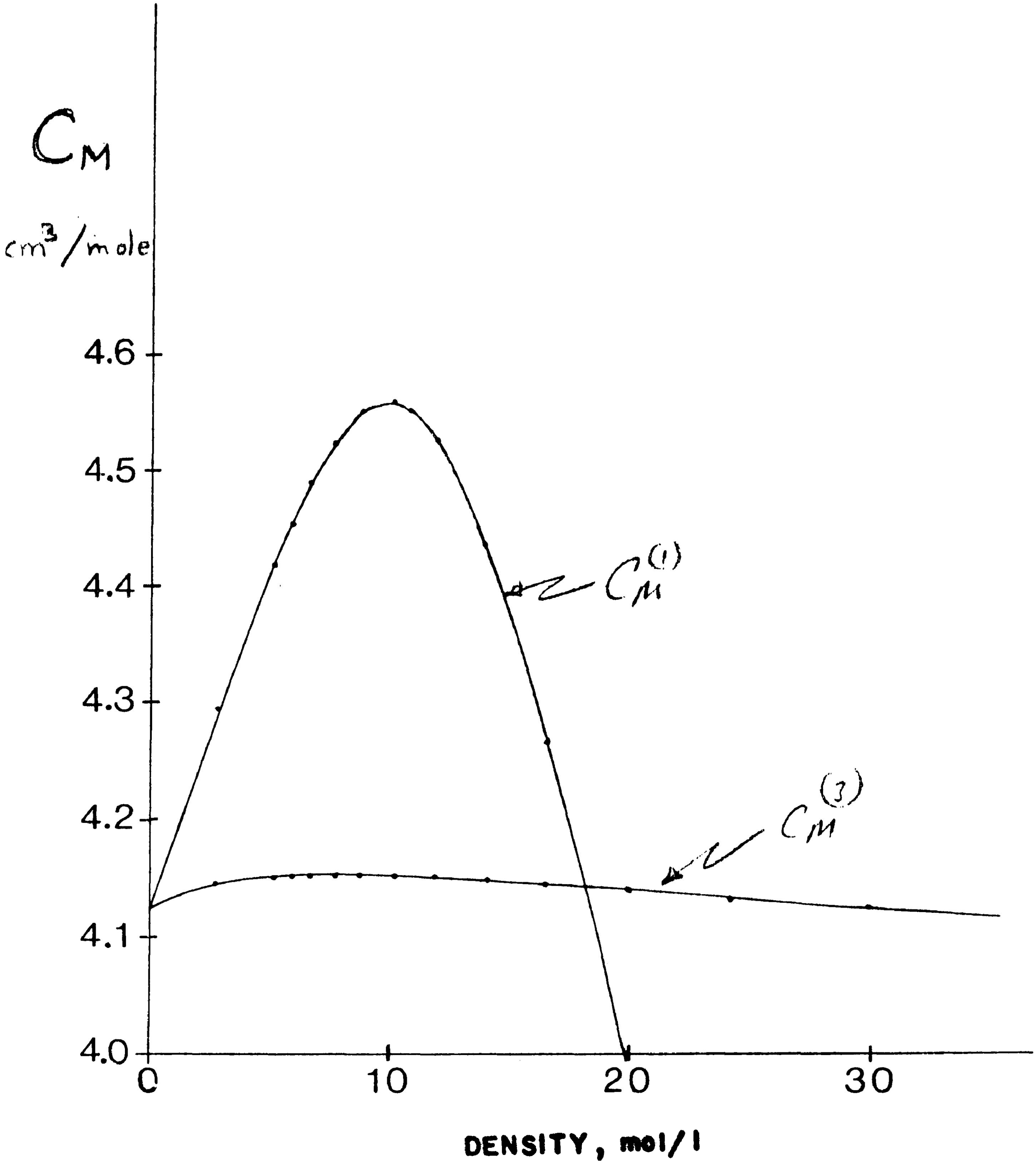

Fig. 30. Comparison of Clausius-Mossotti functions for Argon.
$C_M^{(1)}$, Present theory; $C_M^{(3)}$, Experiment (Ref. [5]).

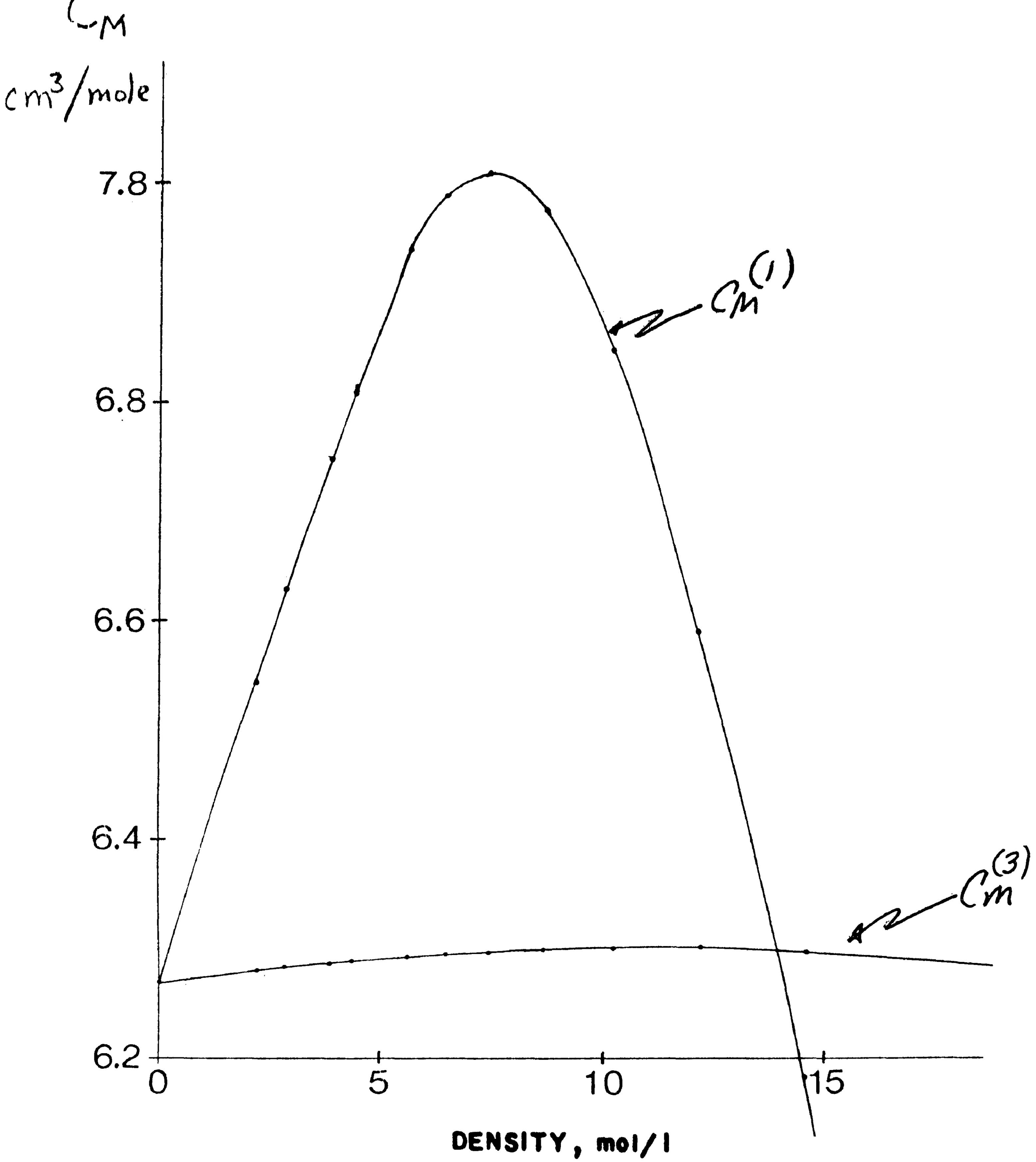

FIG. 31. Comparison of Clausius-Mossotti functions for Krypton.
$C_M^{(1)}$, Present theory; $C_M^{(3)}$, Experiment (Ref. [10]).

experimentally, but $C_M^{(1)}$ rises too rapidly with increasing density at low densities and falls off too rapidly with density at high densities. It thus appears that the dipolar forces between a given molecule and all others in the medium are too strong at low densities and the repulsive forces (arising from the δ-like potential at the "dielectric radius", x_o) are too strong at high densities.

In Sec. VIII we discuss the present model and are led to suggest a new model which, we feel, should lead to a better "continuum-type" theory for the C_M function.

VIII. DISCUSSION AND FUTURE PROPOSALS

Starting from a knowledge of the properties of an isolated, nonpolar atom (treated here as a simple harmonic oscillator), we have attempted in this thesis to discuss in a general way the forces acting on the valence electron(s) when the atom is surrounded by like particles at nonvanishing concentrations, as in a dense gas or fluid.

Our model is based on a "continuum" point of view in that the medium surrounding a given atom has been treated as a homogeneous, isotropic substance characterized by a certain dielectric constant, ε. We have recognized that the reaction potential of the instantaneous atomic dipole tends to attract the valence electrons away from the core while the repulsive potential, which is operative when these electrons are close to a nearest neighbour atom, tends to repel them back toward the core.

We argued that these two forces could account in a qualitative way for the density dependence of the Clausius-Mossotti function C_M. However, on closer inspection, it was found difficult to formulate this approach quantitatively in three-dimensions (Sec. II) because of the *explicit* appearance in the self-energy of the dielectric constant, which is the very quantity we desire to calculate. A further difficulty was the divergence of the self-energy at the dielectric radius, a, of the sphere containing the atom.

(a) The Present Model

These difficulties disappeared, however, when we considered the equivalent one-dimensional problem (Sec. III), for although the permittivity appeared in the back-reaction of the medium, it did so only *implicitly* through the polarization, P, the calculation of which is the main object of this thesis.

With the aid of a computer it was then possible to find the wave functions and energies of a one-dimensional, simple harmonic oscillator restricted by a δ-like repulsive potential at its boundaries (Sec. IV). These same quantities were also calculated for the restricted, one-dimensional oscillator experiencing dipolar interaction with all others in the surrounding medium (Sec. V). The computer is a natural tool for both these cases since we are concerned with the motion of an electron confined to a finite region in space and it is easy to discretize the interval concerned.

Our main result has been the calculation of the ground state polarizability of the one-dimensional, restricted, simple harmonic oscillator interacting through dipolar forces with the surrounding medium (Sec. V), and here we achieved qualitative agreement with experiment in that the C_M-function at first increased with increasing density at low densities, went through a maximum, and then decreased with further increase of density.

When we extended our calculation to try to predict the temperature dependence of the C_M-function (Sec. VI), difficulties occurred in the oscillator model since the spacing of the energy levels at any density is so large compared to kT that dC_M/dT was entirely negligible. The oscillator model thus precludes useful calculations of properties relating to excited states, such as, for example, $C_M(T)$ or the oscillatory contribution to the specific heat of the medium.

The basic difficulty here is that oscillator-like potentials are too *concave* compared with the potentials of real atoms, which are *convex* for valence electrons in excited levels. For this reason not too much significance is to be attached to the calculations of the excited state polarizabilities, $\alpha^{(n)}$ discussed in Sec. VI. However, relative errors in employing the oscillator model for the ground state must be small and should lead to reasonable values for $\alpha^{(o)}$.

An interesting feature of the computer calculation of $\alpha^{(n)}$ has been the possibility of *negative* polarizabilities of excited levels at sufficiently high densities. This result is a direct consequence of the oscillator model which, as explained above, is not to be taken too seriously for the excited states. However, a negative value of $\alpha^{(n)}$ does remind us of an important omission in this model, as well as in all others discussed in Sec. II. This omission concerns the lack of a continuum state for the electron and is a direct result of assuming an infinite potential barrier at the dielectric radius. Such a feature precludes the existence of fully delocalized electronic states in the medium and may be a serious oversight, particularly at high densities.

For any model there should be a *finite* potential barrier for the valence electron(s) and as density is increased we should expect the overlap of potentials of neighbouring atoms to decrease the barrier height. With a finite barrier in the one-dimensional, oscillator model, for example, the wave functions and energies would be different from those calculated here and consequently the polarizabilities would also differ from those found in Sec. VI. There would, in addition, be a finite number, N of excited states possible and one could argue that N and the barrier height should be chosen consistently with the *non*-appearance of negative $\alpha^{(n)}$ for all $1 \leq n \leq N$. An additional effect in such a model would be that the dipolar forces between atoms are screened by the existence of a finite density of free electrons at any given temperature and particle density. Such screening would tend to decrease the dipolar interaction between atoms and could result in a slower increase of C_M with increasing density than found with the present model.

(b) Future Proposals

From what has been said above, it is clear that the model discussed here is unsatisfactory in that:

(i) an oscillator-like potential is unsuitable for calculating properties associated with excited states,

(ii) the model lacks a finite activation energy for the valence electron(s) (even at zero density), and thus does not permit the existence of the ionized state of the atom.

In a better model it is also desirable to work in three-dimensions and to this end we return to (II:13) and note firstly that the coefficients $B_N(\varepsilon)$ in the self-energy of the valence electron in its own reaction field are very insensitive to the permittivity. Inspection shows that:

$$0.75 \leq B_n(\varepsilon) \leq 1$$

for all $0 \leq n \leq \infty$ and all $1 \leq \varepsilon \leq \infty$. For this reason we may, as a reasonable approximation, select $B_n(\varepsilon) \simeq 1$ in which case (II:13) sums to give:

$$V_{\underline{self}} = -\frac{e^2}{a}\left(\frac{\varepsilon-1}{2\varepsilon+1}\right)\cdot\frac{(r/a)^2}{1-(r/a)^2} \qquad \text{(VIII:1)}$$

To (VIII:1) we must now add the atomic potential, $V_a(r)$ of the valence electron in the isolated atom to give an effective potential when the atom is surrounded by others at finite concentration. The result is shown by the dashed curve of Fig. 32 for say $V_a(r) = e^2/r$ (≡ coulomb potential). There is clearly a maximum in this potential given by $V_{\underline{max}}$ at $r = r_{\underline{max}}$.

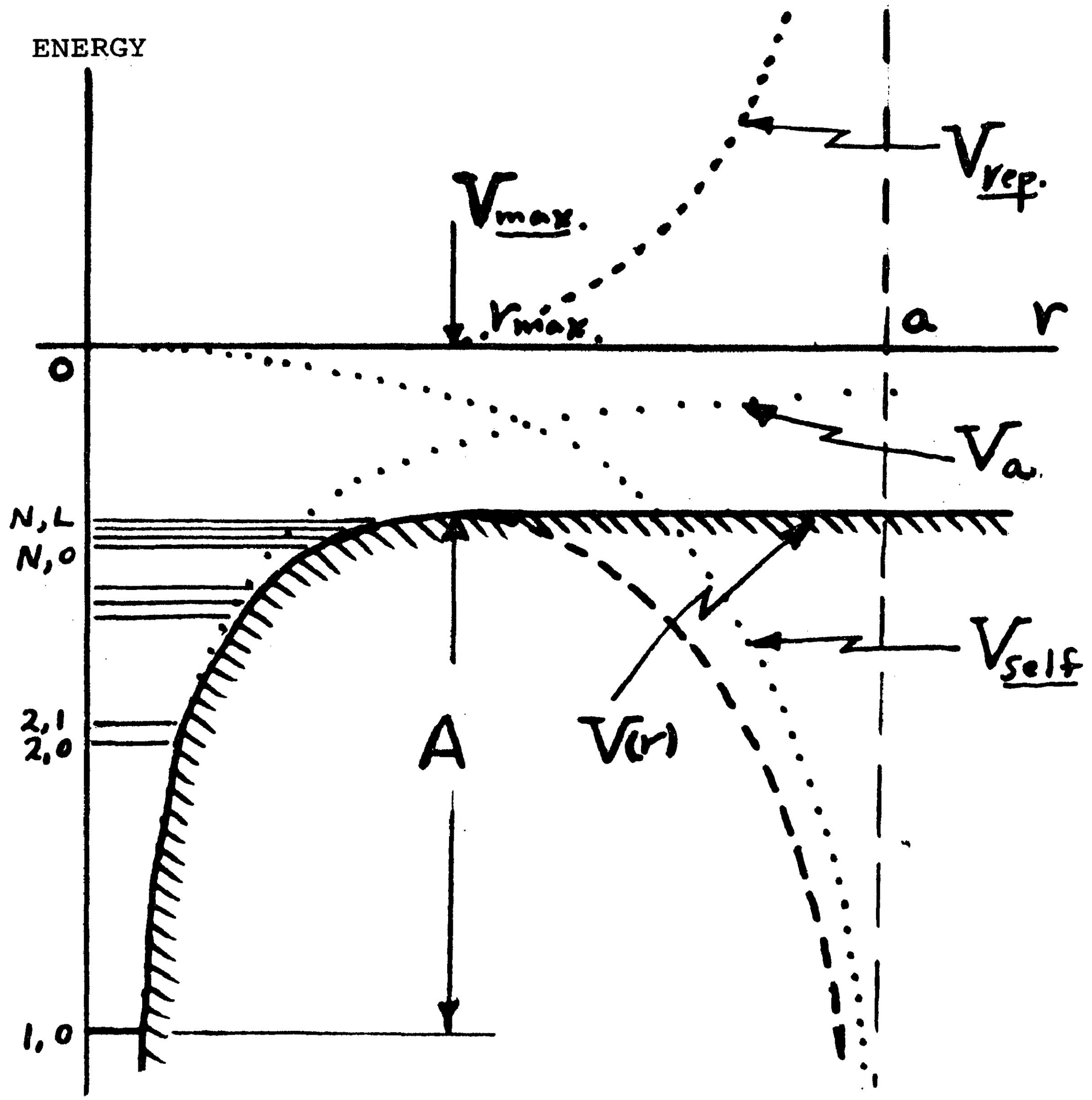

FIG. 32

The difficulty of the negative infinity at $r = a$ could now be overcome by assuming the existence of a repulsive potential:

$$V_{\underline{rep}}(r) = \begin{cases} 0 , & 0 \leq r \leq r_{\underline{max}} \\ -\left[V_{\underline{self}}(r) - V_{\underline{max}}\right] , & r_{\underline{max}} \leq r \leq \infty \end{cases} \qquad \text{(VIII:2)}$$

and the final total potential of a valence electron would be:

$$V(r) = \begin{cases} V_a(r) + V_{\underline{self}}(r) , & 0 \leq r \leq r_{\underline{max}} \\ V_{\underline{max}} , & r_{\underline{max}} \leq r \leq \infty \end{cases} \qquad \text{(VIII:3)}$$

$V(r)$ is indicated in Fig. 32 by the hatched line.

Fig. 32 may be taken to depict the situation at some intermediate density and to actually calculate the shape of $V(r)$, given $V_a(r)$, we could employ as a first approximation a value for $(\varepsilon-1)/(2\varepsilon+1)$, occurring in (VIII:1), given by the unrefined Clausius-Mossotti formula (II:7) for a single molecule. In this way it may easily be seen that:

$$\frac{\varepsilon-1}{2\varepsilon+1} \approx \frac{\alpha_o/a^3}{1+\alpha_o/a^3} \qquad \text{(VIII:4)}$$

At low densities $V_{\underline{max}}$ will be small and $r_{\underline{max}} (\leq a)$ will be large and there will be negligible error in assuming the activation energy, A to be that of the isolated atom. In this case there will be a large number of excited states and the polarizability of the atom will be only slightly higher than that of the isolated atom. Screening for this case would also be negligible as the activation energy is so large compared with kT that very few free electrons would exist at ordinary temperatures.

However, as the density increases $V_{\underline{max}}$ would increase and A and $r_{\underline{max}}$ would decrease and the energy levels would begin to rise above their values of the atom in isolation. There would thus be a general increase of the polarizability of the atom as density increases at low densities. For sufficiently low densities screening would still be unimportant, but as density is increased, and A continues to decrease, there will come a point (probably rather suddenly) at which sufficient free electrons will be present at ordinary temperatures that screening of the dipolar forces between atoms will become important. We might expect this point to be reached when the screening radius $r_s = (kT/4\pi n_e e^2)^{\frac{1}{2}}$ is of the same order as the dielectric radius a. Here $n_e(\rho ,T)$ is the number density of free electrons.

When screening is important the self-energy (VIII:1) would have to be modified as shown by Frood [31] and in this situation it might be expected that the number of excited states, $N(\rho,T)$ will be rather small. The polarizability of the particle would then be smaller than its value for the isolated atom and would continue to decrease as density is further increased.

The above remarks outline qualitatively how $\alpha(\rho,T)$ could change with density in a manner comparable to what is observed experimentally. A calculation based on the above ideas in which at every density quantities such as the activation energy, $A(\rho,T)$, the number of excited states, $N(\rho,T)$, the free electron density, $n_e(\rho,T)$ and the permittivity, $\varepsilon(\rho,T)$ are all mutually self-consistent would be interesting to perform with the aid of a computer.

It may be noted here that the reduction in polarizability envisioned at high densities in this proposed model is directly connected with a reduction in the number of excited states possible as density increases - rather than through increasing confinement of the electron to a "cage" as assumed in the present theory, or those of Ten Seldam et al (loc. cit.).

A complication which must be taken into account is that the polarizability $\alpha^{(n,\ell)}$ of an electron (with principal and orbital quantum numbers n and ℓ) together with the number density, $N^{(n,\ell)}$ of atoms in that level must be non-catastrophic, i.e.

$$1 - \alpha^{(n,\ell)} g^{(n,\ell)} \geq 0 \qquad \text{(VIII:5)}$$

where

$$g^{(n,\ell)} = \frac{4\pi}{3} \frac{2(\varepsilon-1)}{2\varepsilon+1} N^{(n,\ell)}$$

is the reaction field factor for the level (n,ℓ). As shown by Frood (loc. cit.) in connection with impurity conduction, (VIII:5) is the condition which determines the maximum quantum numbers $N(\rho,T)$ and $L(\rho,T)$ which can exist at a given density and temperature.

The foregoing remarks are closely related with the possible appearance of the metallic state in a sufficiently dense medium. Experimentally, it may thus be of interest to examine dielectric and/or conduction losses in very dense nonpolar gases as well as the static or low frequency behaviour of the Clausius-Mossotti function $C_M(\rho,T)$.

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APPENDICES A,B,C AND D
FOR THESIS:

STATIC DIELECTRIC PROPERTIES OF AN ENSEMBLE OF RESTRICTED ONE-DIMENSIONAL OSCILLATORS

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APPENDIX A

```
1000 REM   THIS PROGRAM IS WRITTEN IN MICROSOFT BASIC FOR NORTH STAR
           HORIZON COMPUTER, THIS PROGRAM RUN IN COMPILED BASIC.
1050 REM
1100 REM   PURPOSE : TO CALCULATE EIGEN-ENERGIES OF A BOUND STATE OF ONE
                     DIMENSIONAL SCHRODINGER EQUATION, WITH THE CONDITION
                     THAT THE WAVE FUNCTION VANISHES AT BOUNDARY POINTS.
1150 REM
1200 REM             THE BOUNDARY POINTS WILL BE Y1 AND Y2.
1250 REM
1300 REM             NOTE: THE POTENTIAL ENERGY FUNCTION MUST BE A
                           CONTINUOUS FUNCTION (BOUND STATE).
1350 REM                   THE DISCRETE EIGENVALUE CAN BE OBTAINED,IF
                           IT IS A BOUND STATE SYSTEM.
1400 REM
1450 REM    THE SCHRODINGER EQUATION OF ONE DIMENSIONAL CASE IS GIVEN BY:
1500 REM
1550 REM                          2       2
1600 REM              -(h^2/2M)*d Z(X)/dX +V(X)*Z(X)=e*Z(X)
1650 REM
1700 REM                Z(X) IS WAVE FUNCTION
1750 REM                V(X) IS POTENTIAL ENERGY
1800 REM                e IS EIGEN-ENERGY
1850 REM
1900 REM    TO SOLVE THIS EQUATION WITH THE COMPUTER, WE HAVE TO TRANSFORM
            THE ABOVE EQUATION INTO DEMENSIONLESS DIFERENTIAL EQUATION.
1950 REM
2000 REM    NOW, CONSIDER A SYSTEM WHICH THE POTENTIAL ENERGY IS GIVEN BY,
            V(X)=0.5*M*w^2*X^2                ( A RESTRICTED OSCILLATOR)
         OR V(X)=0.5*M*w^2*x^2*[1-(wp/w)^2]   ( A RESTRICTED OSCILLATOR WITH
2050 REM                                        DIPOLAR INTERACTION )
2100 REM
2150 REM    TO MAKE THE ABOVE EQUATION BECOMES DEMENSIONLESS DIFFERENTIAL
2200 REM    EQUATION . WE LET,
2250 REM                          Y=X/(h/2Mw)^0.5
2300 REM
2350 REM                          E=e/hw
2400 REM
2450 REM    THEN THE DIFFERENTIAL EQUATION BECOMES,
2500 REM
2550 REM                 2    2
2600 REM               -d Z/dY +V(Y)*Z=E*Z
2650 REM
2700 REM   WHERE: V(Y)=(Y/2)^2                FOR A RESTRICTED OSCILLATOR,
             AND  V(Y)=(Y/2)^2*[1-(wp/w)^2]   FOR A RESTRICTED OSCILLATOR WITH
                                                 DIPOLAR INTERACTION.
2750 REM
           NOTE : IF V(Y)=(Y/2)^2 THEN THE STATEMENT # 4900   SHOULD BE
                  ACTIVATED !!! ELSE THE STATEMENT #   4950   SHOULD BE
                  ACTIVATED.

2800 REM    TO SOLVE THIS EQUATION BY COMPUTER, WE FIRST DISCRETIZE THE
2850 REM    DIFFERENTIAL EQUATION, THEN USE BOUNDARY CONDITION, THAT ARE
            Z=0 AT THE END POINTS(Y=Y1,LEFT END POINT,Y=Y2,RIGHT END POINT).
2900 REM
2950 REM    SINCE   (wp/w)^2=9.0335506E08/[Y2^3*w^0.5]
```

```
          THEREFORE, WE LET V(Y)=(Y/2)^2*(1-903355060#/((Y2^3)*w^.5))))
3000 REM
3050 REM   NOTE : THE ABOVE POTENTIAL IS FOR A RESTRICTED OSCILLATOR WITH
                  DIPOLAR INTERACTION.
3100 REM
3150 REM    THEN ,
3200 REM               -[{(Zi-1)-(2*Zi)+(Zi+1)}/H^2]+V(Yi)*Zi=E*Zi
3250 REM
3300 REM               AND        H=(Y2-Y1)/(N+1)
3350 REM
3400 REM         WHERE, N IS THE NUMBER OF POINT BETWEEN TWO END POINTS.
3450 REM
3500 REM     BY SETTING Z(0)=Z(N+1)=0 . WE OBTAIN,
3550 REM                     [A]|Z>=E*|Z>
3600 REM
                WHERE |Z> IS A EIGENVECTOR WITH ENTRIES Zi  (i=0 to N)
3650 REM
3700 REM                               Aii=2/H^2+V(Yi)   ,  i=1 to N
3750 REM
3800 REM                               Ai+1,i=Ai,i+1=-1/H^2 , i=1 to N-1
3850 REM
3900 REM                               AND OTHERS ARE ZEROS.
3950 REM
4000 DEFDBL A,B,C,S,R,Q,L,Z,M,T,V,H,Y,X,D,E,P,W :'  DECLARE DOUBLE PRECISION.
4050 DEFINT I,J,K,N                        :REM  DECLARE INTEGER.
4100 PRINT  "THE NUMBER OF POINT MUST BE AN ODD NUMBER"
4150 INPUT "THE NUMBER OF POINT IS";N  :REM N IS THE NUMBER OF POINT
                                             BETWEEN THE BOUNDARY POINTS
4200 INPUT "THE VALUE OF Y1";Y1
4250 INPUT "THE VALUE OF Y2";Y2
4300 PRINT " IF THE SYSTEM IS RESTRICTED OSCILLATOR ONLY THEN THE SYSTEM "
4350 PRINT " IS INDEPENDENT OF ANGULAR FREQUENCY"
4400 INPUT "THE ANGULAR FREQUENCY";WO  :REM w=WO
4450 PRINT
4500 PRINT "THE NUMBER OF POINT BETWEEN BOUNDARY POINTS IS" N
4550 PRINT
4600 PRINT "THE LEFT HAND SIDE LIMIT IS =" Y1
4650 PRINT
4700 PRINT "THE RIGHT HAND SIDE LIMIT IS =" Y2
4750 PRINT
4800 PRINT "THE ANGULAR FREQUENCY IS";WO
4850 PRINT
4900 REM   DEF FNV(Y)=(Y/2)^2
4950 DEF FNV(Y)=(.5*Y)^2*(1-(903355060#/((Y2^3)*(WO^.5))))
5000 NZ=N
5050 H=(Y2-1*Y1)/(N+1)                     :REM  H IS LENGTH BETWEEN Yi AND Yi+1.
5100 REM
          MATRIX [A] IS A TRIDIAGONAL MATRIX,THEN WE CAN USE 3 VECTORS FOR
          REPRESENTING MATRIX [A].

5150 DIM A(80),B(80),Q(80)
5200 FOR I=1 TO N                          :REM  THIS LOOP IS USED TO FIND
5250 Y=Y1+I*H                              :REM  THE VALUES OF Yi AND THE
5300 VY=FNV(Y)                             :REM  ENTRIES OF Aii.
```

```
5350 A(I)=2/(H^2)+VY
5400 NEXT I
5450 B(1)=0
5500 Q(N)=0
5550 FOR I=2 TO N
5600 B(I)=-1/(H^2)                     :REM  Bi IS THE SUBDIAGONAL OF [A].
5650 Q(I-1)=-1/(H^2)                   :REM  Qi IS THE SUPERDIAGONAL OF [A].
5700 NEXT I
5750 REM
5800 BZ=B(2)
5850 REM
5900 FOR I=1 TO N
5950 PRINT B(I),A(I),Q(I)
6000 NEXT I
6050 REM                                  FROM STATEMENT #6150-#10450
6100 REM                                  AND THEIR SUB-PROGRAMS(GOSUB)
6150 DIM C(80)                     :REM  IS A PROGRAM TO DIAGONALIZE MATRIX
6200 DIM S(80)                     :REM  [A] USING QR ALGORITHM(REF:PAGE
6250 DIM R(80)                     :REM  425-427 OF NUMERICAL ANALYSIS BY
6300 REM                                  BURDEN ET-AL).
6350 REM
6400 REM                   THE QR PROGRAM THAT WE WROTE IS A SLIGHT
                           MODIFICATION OF QR ALGORITHM(REFERENCE BOOK),
                           THIS IS DUE TO THE NATURE OF OUR PROBLEM.
6450 IF N=2 GOTO 10350
6500 REM                         GOSUB 11400 TO 11800 IS REFERRED TO STEP:3.
6550 GOSUB 11400
6600 FOR I=1 TO N          :REM  FROM STATEMENT #6600-#6900 IS STEP:4
6650 A(I)=A(I)-LMD
6700 C(I)=0
6750 S(I)=0
6800 R(I)=0
6850 Q(I)=0
6900 NEXT I
6950 PI=A(1)               :REM  INITIALIZATION
7000 RO=B(2)               :REM  INITIALIZATION
7050 J=2                   :REM  REFER TO STEP:5.
7100 REM                              FROM STATEMENT #7150-7350 REFERRED TO
7150 A(J-1)=(PI^2+B(J)^2)^.5   :REM  STEP:6.
7200 C(J)=PI/A(J-1)
7250 S(J)=B(J)/A(J-1)
7300 Q(J-1)=C(J)*RO+S(J)*A(J)
7350 PI=-1*S(J)*RO+C(J)*A(J)
7400 IF J=N GOTO 7650            :REM  REFER TO STEP:7.
7450 R(J-1)=S(J)*B(J+1)          :REM  #7450-7500 REFER TO STEP:8
7500 RO=C(J)*B(J+1)              :REM  STEP:9 AND STEP:10 ARE INSIDE STEP:6.
7550 J=J+1                       :REM  REFER TO STEP:11.
7600 IF J<=N GOTO 7150           :REM  REFER TO STEP:12.
7650 A(N)=PI                     :REM  THE LAST ENTRY OF VECTOR A
7700 DIM L(2,2),M(2,2),ML(2,2),Z(2,2),T(2,2)
7750 J=2                         :REM  FROM #7750-#9600 IS STEP:13
7800 IF J=2 GOTO 8650            :REM  THE MATRIX FORM UP TO STEP:12 IS
7850 L(1,1)=Q(J-2)               :REM  UPPER TRIANGULAR MATRIX WITH VECTOR
7900 L(1,2)=R(J-2)               :REM  A,Q,R AS ITS ENTRIES. SINCE THE
7950 L(2,1)=0                    :REM  MATRIX IS REDUCED INTO DIAGONAL
```

```
8000 L(2,2)=0                             :REM  MATRIX BY ORTHOGONAL TRANSFORMATION,
8050 FOR I=1 TO 2                         :REM  SO BY TAKING ADVANTAGE OF THE PROPERTY
8100 FOR K=1 TO 2                         :REM  OF ORTHOGONAL MATRICES WHICH ARE
8150 ML(I,K)=L(I,K)                       :REM  DISCRIBED BY STEP:9(TEXT-BOOK),WE
8200 NEXT K                               :REM  CAN BREAK THESE ORTHOGONAL MATRICES
8250 NEXT I                               :REM  INTO PARTITION MATRICES AND THEN,
8300 Z(1,1)=C(J)                          :REM  MULTIPLY THESE ORTHOGONAL MATRICES
8350 Z(2,1)=S(J)                          :REM  ONE BY ONE.
8400 Z(1,2)=-1*S(J)                   :REM  WHY DO WE USE 2 BY 2 MATRICES IN
8450 Z(2,2)=C(J)                      :REM  THESE MULTIPLICATION ?
8500 GOSUB 10850                      :REM  TO ANSWER THIS QUESTION,WE HAVE TO
8550 Q(J-2)=T(1,1)                    :REM  REFER TO DEFINITION OF ORTHOGONAL
8600 R(J-2)=T(1,2)                    :REM  MATRIX WHICH IS DEFINED IN STEP:9,
8650 M(1,1)=A(J-1)                    :REM  FROM STEP:9(TEXT),WE CONCLUDE THAT
8700 M(1,2)=Q(J-1)                    :REM  THE MATRIX NEEDED FOR THE MULTIPLICATION
8750 M(2,1)=0                         :REM  IS 2 BY 2 MATRICES(SINCE [Q]*[I]=[Q]),
8800 M(2,2)=A(J)                      :REM  WHERE, [Q] IS ANY KIND OF MATRIX AND [I]
8850 FOR I=1 TO 2                     :REM  IS IDENTITY MATRIX.
8900 FOR K=1 TO 2
8950 ML(I,K)=M(I,K)
9000 NEXT K
9050 NEXT I
9100 Z(1,1)=C(J)
9150 Z(2,1)=S(J)
9200 Z(1,2)=-1*S(J)
9250 Z(2,2)=C(J)
9300 GOSUB 10850
9350 A(J-1)=T(1,1)
9400 B(J)=T(2,1)
9450 Q(J-1)=T(1,2)
9500 A(J)=T(2,2)
9550 J=J+1
9600 IF J<=N GOTO 7850
9650 FOR I=1 TO N                     :REM  FROM #9650-#9750 IS STEP:14
9700 A(I)=A(I)+LMD
9750 NEXT I
9800 REM                              :REM  FROM #9800-#10300 IS STEP:2
9850 REM                                    THIS STEP IS NOT EXACTLY THE SAME AS
9900 REM                                    STEP:2 IN THE TEXT BUT IT IS A SLIGHT
9950 REM                                   DIFFERENT FROM TEXTBOOK,THIS DUES TO THE
10000 REM                                   NATURE OF OUR PROBLEM.
10050 REM CHECK B(N) IS LESS THAN 1.E-10
10100 REM
10150 BN1=B(N-1)
10200 BN=B(N)
10250 IF ABS(BN)<=1E-10 THEN N=N-1 :GOTO 6400
10300 IF ABS(BN1)<=1E-10 THEN GOSUB 11400 :A(N)=XL1 :A(N-1)=XL2
                          :N=N-2 :GOTO 6400 ELSE GOTO 6400
10350 FOR I=1 TO NZ
10400 PRINT "THE VALUE OF DIAGONAL MATRIX IS =A("I")"  A(I)
10450 NEXT I
10500 REM
10550 OPEN "O",#1,"EIGENERG"          :REM  THE RESULT OF QR PROGRAM IS
10600 FOR I=1 TO NZ                   :REM  STORED IN THE DISC WITH THE
10650 PRINT#1,A(I)                    :REM  SEQUENTIAL FILE.
```

```
10700 NEXT I
10750 CLOSE#1
10800 END
10850 FOR I=1 TO 2                                    :REM  #10850-#11300 IS A SUBPROGRAM
10900     FOR J1=1 TO 2                               :REM  OF 2 BY 2 MATRIX MULTIPLICATION
10950     SUM=0                                       :REM  OF MATRIX ML AND MATRIX Z.
11000         FOR K=1 TO 2
11050         SUM=SUM+ML(I,K)*Z(K,J1)
11100         NEXT K
11150         T(I,J1)=SUM
11200     NEXT J1
11250 NEXT I
11300 RETURN
11350 REM  FROM #11400 TO #11800 IS A SUBPROGRAM TO CALCULATE THE
           EIGENVALUES OF THE LAST 2 BY 2 MATRIX OF MATRIX [A].
           SO THE EIGENVALUES WILL BE THE ROOTS OF QUADRATIC EQN.
11400 AN=A(N)+A(N-1)                           :REM AN AND ABN IS THE COEFFICIENT OF THE
11450 ABN=A(N)*A(N-1)-B(N)*Q(N-1)              :REM  QUADRATIC EQN SUCH THAT
                                                     X^2-AN*X+ABN=0.
11500 RN=AN^2-4*ABN                            :REM THEORITICALLY,RN>=0,AND COMPUTER
                                                    DO APPROXIMATION,SO WE EXPECT
                                                    RN<0,AND IT NEGLIGIBLE COMPARE TO
11550 REM                                           THE ROOTS.
11600 IF RN<0 THEN PRINT "THE D IS =" RN,"THE ROOT ="AN/2
                 :PRINT "B("N")=" B(N),"B("N-1")=" B(N-1)
           : IF ABS(RN)<.09 THEN LMD=AN/2 :GOTO 11800
11650 XL1=(AN+(RN^.5))/2                       :REM  XL1 AND XL2 IS THE ROOTS
11700 XL2=(AN-(RN^.5))/2                       :REM  LMD IS THE NEW EIGENVALUE.
11750 IF ABS(A(N)-XL1)<=ABS(A(N)-XL2) THEN LMD=XL1 ELSE LMD=XL2
11800 RETURN
```

APPENDIX B

```
1000 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
1050 '      THIS PROGRAM IS WRITTEN IN MICROSOFT BASIC FOR NORTH STAR
1100 '      HORIZON COMPUTER. THIS PROGRAM RUN IN COMPILED BASIC.
1150 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
1200 '
1250 '      THIS PROGRAM CALCULATES AND STORES THE FIRST EIGHT EIGEN-
1300 '      ENERGIES AND EIGEN-VECTORS OF THE RESTRICTED OSCILLATOR
1350 '      WITH OR WITHOUT DIPOLAR INTERACTION.
1400 '
1450 '      ACTUALLY, FOR A GIVEN EIGEN-ENERGY, WE CAN CALCULATE THE
1500 '      CORRESPONDING EIGEN-VECTOR. HOWEVER, THE CALCULATED EIGEN-
1550 '      ENERGIES FROM PROGRAM WHICH IS LISTED IN APPENDIX A ARE NOT
1600 '      ACCURATE, AND THE EXACT EIGEN-ENERGY WILL BE SOMEWHERE IN
1650 '      THE NEIGBOURHOOD OF THE CALCULATED EIGEN-ENERGY.
1700 '      THUS, BY SHIFTING CALCULATED EIGEN-ENERGY TO LEFT AND RIGHT,
1750 '      ONE CAN OBTAIN THE NEARLY EXACT EIGEN-ENERGY AND ITS
1800 '      CORRESPOND EIGEN-VECTOR.
1850 '      HERE, WE USE THE SAME MATRIX [A] AS USED IN THE PROGRAM WHICH
1900 '      IS LISTED IN APPENDIX A AND ALSO USE THE CALCULATED EIGEN-
1950 '      ENERGY TO GET A BETTER APPROXIMATION OF EIGEN-ENERGY.
2000 '
2050 '      NOTE: THIS PROGRAM IS INSEPERABLE FROM PROGRAM WHICH IS
2100 '            LISTED IN APPENDIX A. THAT IS, AFTER WE GET THE
2150 '            CALCULATED EIGEN-ENERGY FROM PROGRAM (APPENDIX A),
2200 '            WE USE THIS RESULT AS OUR INPUT IN THIS PROGRAM.
2250 '
2300 REM
2350 DEFDBL A,B,C,E,Q,R,Y,W,D,V,X,H,M,S,Z
2400 DEFINT I,J,K,N                          :REM  DECLARE INTEGER.
2450 PRINT  "THE NUMBER OF POINT MUST BE AN ODD NUMBER"
2500 INPUT "THE NUMBER OF POINT IS";N   :REM N IS THE NUMBER OF POINT
                                              BETWEEN THE BOUNDARY POINTS
2550 INPUT "THE VALUE OF Y1";Y1
2600 INPUT "THE VALUE OF Y2";Y2
2650 PRINT "IF THE SYSTEM IS RESTRICTED OSCILLATOR WITHOUT DIPOLAR"
2700 PRINT "INTERACTION THEN THE STATEMENT #3450 SHOULD BE "
2750 PRINT "ACTIVATED AND #3500 SHOULD BE DEACTIVATED"
2800 PRINT "ALSO, THE DIMENSIONLESS POTENTIAL ENERGY INDEPENDENT"
2850 PRINT "OF FREQUENCY WO, SO WE CAN WRITE WO=SOME VALUE"
2900 INPUT "THE ANGULAR FREQUENCY IS";WO  :REM w=WO
2950 PRINT
3000 PRINT "THE NUMBER OF POINT BETWEEN BOUNDARY POINTS IS" N
3050 PRINT
3100 PRINT "THE LEFT HAND SIDE LIMIT IS =" Y1
3150 PRINT
3200 PRINT "THE RIGHT HAND SIDE LIMIT IS =" Y2
3250 PRINT
3300 PRINT "THE ANGULAR FREQUENCY IS";WO
3350 PRINT
3400 PRINT
3450 REM DEF FNV(Y)=(Y/2)^2
3500 DEF FNV(Y)=(.5*Y)^2*(1-(903355060#/((Y2^3)*(WO^.5))))
3550 NZ=N                                    :REM  NZ WILL BE USED LATER.
3600 H=(Y2-1*Y1)/(N+1)                       :REM  H IS LENGTH BETWEEN Yi AND Yi+1.
3650 REM
```

```
3700 REM      MATRIX [A] IS A TRIDIAGONAL MATRIX,THEN WE CAN USE 3 VECTORS FO
              REPRESENTING MATRIX [A].
3750 REM
3800 DIM A(80),B(80),Q(80),A1(80),A2(80),WF(80),WG(80),EG(10)
3850 DIM WN(80),DZ(80),DP(80),XZ(80),YZ(80),ZJ(10)
3900 FOR I=1 TO N                  :REM  THIS LOOP IS USED TO FIND
3950 Y=Y1+I*H                      :REM  THE VALUES OF Yi AND THE
4000 VY=FNV(Y)                     :REM  ENTRIES OF Aii.
4050 A(I)=2/(H^2)+VY
4100 NEXT I
4150 B(1)=0
4200 Q(N)=0
4250 FOR I=2 TO N
4300 B(I)=-1/(H^2)                 :REM  Bi IS THE SUBDIAGONAL OF [A].
4350 Q(I-1)=-1/(H^2)               :REM  Qi IS THE SUPERDIAGONAL OF [A].
4400 NEXT I
4450 REM
4500 FOR I=1 TO NZ                 :REM  THIS A1(I) IS NEEDED LATER.IE,
4550 A1(I)=A(I)                    :REM  FOR CALCULATE THE WAVE FUNCTION
4600 NEXT I                        :REM  AFTER THE EIGENVALUE ARE OBTAINED.
4650 HZ=H
4700 BZ=B(2)
4750 REM
4800 FOR I=1 TO N
4850 PRINT B(I),A(I),Q(I)
4900 NEXT I
4950 OPEN "I",#1,"EIGENERG"      :REM  ACCESS TO THE FILE WHICH CONTAINS
5000 FOR I=1 TO N                :'    EIGEN-ENERGY. THIS EIGEN-ENERGY
5050 INPUT#1,A(I)                :'    WAS CALCULATED BY THE COMPUTER
5100 NEXT I                      :'    (SEE APPENDIX A)
5150 I=1
5200 GOSUB 11850
5250 IF IFLAG=1 GOTO 5400
5300 IF IND=0 THEN GOSUB 14350  ELSE GOSUB 17400
5350 IF IFLAG=0 THEN PRINT "NO RESULT" :STOP
5400 FOR J=0 TO NZ+1
5450 WF(J)=WN(J)
5500 NEXT J
5550 A(I)=ERG                    :' STORE NEARLY EXACT EIGENVALUE IN A(I)
5600 PRINT "THE VALUE OF I IS="I
5650 '
5700 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
5750 '     THIS SECTION STORES THE NEARLY EXACT GROUND STATE WAVE
5800 '     FUNCTION.
5850 '
5900 OPEN "O",#2,"WAVEFCN1"
5950 FOR J=0 TO NZ+1
6000 PRINT #2,WF(J)
6050 NEXT J
6100 CLOSE #2
6150 '
6200 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
6250 '
6300 FOR I=2 TO NZ
6350 ITS1=I/2
```

```
6400 ITS2=2*ITS1
6450 IF I=ITS2 THEN GOSUB 12750 ELSE GOSUB 11850
6500 IF IFLAG=1 GOTO 6650
6550 IF IND=0 THEN GOSUB 14350 ELSE GOSUB 17400
6600 IF IFLAG=0 THEN PRINT "NO RESULT" :STOP
6650 FOR J=0 TO NZ+1
6700 WG(J)=WN(J)
6750 NEXT J
6800 A(I)=ERG                 :'  STORE EIGEN-ENERGY IN VECTOR A(I)
6850 PRINT "THE VALUE OF I IS="I
6900 IF I=2 THEN GOSUB 21000
6950 IF I=3 THEN GOSUB 21300
7000 IF I=4 THEN GOSUB 21600
7050 IF I=5 THEN GOSUB 21900
7100 IF I=6 THEN GOSUB 22200
7150 IF I=7 THEN GOSUB 22450
7200 IF I=8 THEN GOSUB 22750
7250 IF I=8 GOTO 7350
7300 NEXT I
7350 GOSUB 24200
7400 END
7450 '*******************************************************************
7500 '     THIS SECTION CALCULATE THE UN-NORMALIZED EIGEN-VECTOR
7550 '     BY ASSIGNING THE FIRST ENTRY OF EIGEN-VECTOR WN(1)=1 OR -1.
7600 '     NOTE: WN(1)=1 WHEN THE WAVE FUNCTION HAS EVEN PARITY AND
7650 '           WN(1)=-1 WHEN THE WAVE FUNCTION HAS ODD PARITY.
7700 '
7750 REM
7800 FOR K=1 TO NZ
7850 A2(K)=A1(K)-ERG
7900 NEXT K
7950 ITS1=I/2  :ITS2=2*ITS1
8000 IF ITS2=I THEN S1=-1 :S2=A2(1)/BZ :GOTO 8150
8050 S1=1
8100 S2=-1*(A2(1)/BZ)
8150 WN(1)=S1  :WN(2)=S2
8200 K=2
8250 S3=-1*(BZ*S1+A2(K)*S2)/BZ
8300 WN(K+1)=S3
8350 S1=S2
8400 S2=S3
8450 K=K+1
8500 IF K<=(NZ-1) GOTO 8250
8550 WN(0)=0 :WN(NZ+1)=0
8600 RETURN
8650 '
8700 '*******************************************************************
8750 '
8800 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
8850 '    THIS SECTION CALCULATE THE INTEGRAL USING SIMPSON'S RULE.
8900 '
8950 K=1
9000 AR=DZ(0)+DZ(NZ+1)+4*DZ(K)
9050 NN=(NZ+1)/2
9100 FOR K=2 TO NN
```

```
9150 KZ=2*K
9200 ARH=4*DZ(KZ-1)+2*DZ(KZ-2)
9250 AR=AR+ARH
9300 NEXT K
9350 ARE=(HZ/3)*AR
9400 RETURN
9450 '
9500 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
9550 REM
9600 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
9650 '     THIS SECTION CALCULATE THE PROBABILITY DENSITY.
9700 REM
9750 FOR J=0 TO NZ+1
9800 DZ(J)=WN(J)*WN(J)
9850 NEXT J
9900 RETURN
9950 '
10000 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
10050 '
10100 '##############################################################
10150 '     THIS SECTION CALCULATE THE NORMALIZED WAVE FUNCTION.
10200 '
10250 ARA=ARE
10300 CN=ARA^-.5          :REM CN IS NORMALIZED CONSTANT
10350 FOR J=0 TO NZ+1
10400 WN(J)=CN*WN(J)
10450 YZ(J)=WN(J)
10500 NEXT J
10550 RETURN
10600 '
10650 '##############################################################
10700 '
10750 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
10800 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
10850 '     THIS SECTION DETERMINE WHEATHER THE NEARLY EXACT EIGEN-
10900 '     ENERGY IS ON THE LEFT/RIGHT HAND SIDE OF THE CALCULATED
10950 '     EIGEN-ENERGY WHICH IS COMPUTED BY PREVIOUS PROGRAM
11000 '     (APPENDIX A).
11050 '     HERE, WE ASSUME THAT THE WAVE FUNCTION HAS SYMMETRY
11100 '     ABOUT THE ORIGIN. FOR EVEN FUNCTION, CP IS THE DIFFERENT
11150 '     OF THE WAVE FUNCTION WHICH ARE EVALUATED AT POINTS
11200 '     y1 AND yN. FOR ODD FUNCTION, CP IS THE WAVE FUNCTION WHICH
11250 '     IS EVALUATED AT THE ORIGIN.
11300 '     IFLAG AND IND ARE INDICATORS.
11350 '     WHEN IFLAG=1 INDICATES THAT THE NEARLY EXACT EIGEN-ENERGY
11400 '     AND ITS WAVE FUNCTION HAVE BEEN OBTAINED.
11450 '     WHEN IND=0 INDICATES THE EXACT EIGEN-ENERGY LIES ON THE
11500 '     LEFT HAND SIDE OF THE CALCULATED EIGEN-ENERGY (APPENDIX A).
11550 '     WHEN IND=1 INDICATES THE EXACT EIGENVALUE LIES ON THE RIGHT
11600 '     HAND SIDE OF THE CALCULATED EIGEN-ENERGY (APPENDIX A).
11650 '
11700 '###############################################################
11750 '      THIS SUBSECTION FOR THE WAVE FUNCTION HAS EVEN PARITY.
11800 '
11850 IFLAG=0
```

```
11900 ERG=A(I)
11950 GOSUB 7800 :GOSUB 9750 :GOSUB 8950 :GOSUB 10250
12000 CP=ABS(WN(1)-WN(N))
12050 IF CP<=1E-08 THEN IFLAG=1 :GOTO 12400
12100 CP1=CP
12150 ERG=ERG+.000005
12200 GOSUB 7800 :GOSUB 9750 :GOSUB 8950 :GOSUB 10250
12250 CP=ABS(WN(1)-WN(N))
12300 IF CP<=1E-08 THEN IFLAG=1 :GOTO 12400
12350 IF CP>CP1 THEN IND=0 ELSE IND=1
12400 RETURN
12450 '
12500 '#############################################################
12550 '
12600 '?????????????????????????????????????????????????????????????
12650 '     THIS SUBSECTION FOR THE WAVE FUNCTION HAS ODD PARITY.
12700 '
12750 IFLAG=0
12800 ERG=A(I)
12850 GOSUB 7800 :GOSUB 9750 :GOSUB 8950 :GOSUB 10250
12900 N1=(N+1)/2
12950 CP=WN(N1)
13000 IF ABS(CP)<=1E-08 THEN IFLAG=1 :GOTO 13500
13050 CP1=CP
13100 ERG=ERG+.000005
13150 GOSUB 7800 :GOSUB 9750 :GOSUB 8950 :GOSUB 10250
13200 CP=WN(N1)
13250 IF (CP<0) XOR (CP1<0) THEN IND=1 :GOTO 13500
13300 IF CP<0 GOTO 13450
13350 IF CP <CP1 THEN IND=1 ELSE IND=0
13400 GOTO 13500
13450 IF ABS(CP) < ABS(CP1) THEN IND=1 ELSE IND=0
13500 RETURN
13550 '
13600 '????????????????????????????????????????????????????????????????
13650 '
13700 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
13750 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
13800 '    MOST OF THE CALCULATION OF FINDING THE NEARLY EXACT EIGEN-
13850 '    VALUE AND ITS EIGEN-VECTOR ARE IN THIS SECTION.
13900 '
13950 '    HERE, WE ASSUME THAT FOR A RANGE OF ENERGIES WHICH ARE IN
14000 '    THE NEGHBOURHOOD OF CALCULATED EIGENVALUE, THE CC'S OR CP'S
14050 '    VALUES FORM  A CONCAVE CURVE.
14100 '
14150 '+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
14200 '
14250 '                    FOR  IND=0
14300 '
14350 IFLAG=0
14400 INC=0
14450 ITS1=I/2
14500 ITS2=2*ITS1
14550 N1=(N+1)/2
14600 IF Y2 > 3.6 GOTO 14850
```

```
14650 TT=.01
14700 IF I=3 THEN TT=.0001               :'  TT IS A DE/INCREMENT.
14750 IF I>=4 THEN TT=.000001            :'  SINCE THE EIGEN-ENERGY
14800 GOTO 15250                         :'  WHICH CALCULATED BY
14850 IF Y2 > 5 GOTO 15100               :'  PREVIOUS PROGRAM HAS
14900 TT=.001                            :'  BETTER ACCURACY AS I
14950 IF I=3 THEN TT=.00001              :'  INCREASES. THEREFORE, TT
15000 IF I>=4 THEN TT=.000001            :'  BECOMES SMALLER AS I INCREASES.
15050 GOTO 15250
15100 TT=.0001
15150 IF I=3 THEN TT=.000001
15200 IF I>=4 THEN TT=.0000001
15250 EL=A(I)-TT
15300 EH=A(I)
15350 ERG=EL
15400 IF INC>1000  THEN PRINT "EXIT THE LIMIT" :STOP
15450 HE=(EH-EL)/10
15500 FOR J8=0 TO 10
15550 ERG=ERG+J8*HE
15600 EG(J8)=ERG
15650 GOSUB 7800 :GOSUB 9750 :GOSUB 8950 :GOSUB 10250
15700 IF I=ITS2 THEN GOSUB 23550 :GOTO 16000
15750 CP=ABS(WN(1)-WN(N))
15800 IF CP<=1E-08 THEN IFLAG=1 :GOTO 17000
15850 ZJ(J8)=CP
15900 PRINT "CP("J8")="ZJ(J8)
15950 GOTO 16200
16000 CC=WN(N1)
16050 IF ABS(CC)< 1E-08 THEN IFLAG=1 :GOTO 17000
16100 ZJ(J8)=ABS(CC)
16150 PRINT "CC("J8")="ZJ(J8)
16200 NEXT J8
16250 CMIN=ZJ(0)
16300 J1=0
16350 FOR K=1 TO 10
16400 IF ZJ(K) < CMIN THEN CMIN=ZJ(K) :J1=K
16450 NEXT K
16500 PRINT "INC IS="INC
16550 KW=J1
16600 KQ=KW-1
16650 KP=KW+1
16700 IF J1=0 THEN EH=EL :EL=EL-TT :INC=INC+1 :GOTO 15350
16750 EL=EG(KQ)
16800 EH=EG(KP)
16850 IF (EH-EL)<1E-15 THEN PRINT "THE ASSUMPTION IS WRONG" :STOP
16900 ERG=EL
16950 GOTO 15450
17000 RETURN
17050 '
17100 '+++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
17150 '
17200 '@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
17250 '
17300 '                         FOR IND=1
17350 '
```

```
17400 INC=0
17450 IFLAG=0
17500 ITS1=I/2
17550 ITS2=2*ITS1
17600 N1=(N+1)/2
17650 IF Y2 > 3.6 GOTO 17900
17700 TT=.01
17750 IF I=3 THEN TT=.0001
17800 IF I>=4 THEN TT=.000001
17850 GOTO 18300
17900 IF Y2 > 5 GOTO 18150
17950 TT=.001
18000 IF I=3 THEN TT=.00001
18050 IF I>=4 THEN TT=.000001
18100 GOTO 18300
18150 TT=.0001
18200 IF I=3 THEN TT=.000001
18250 IF I>=4 THEN TT=.0000001
18300 EL=A(I)
18350 EH=A(I)+TT
18400 ERG=EL
18450 IF INC > 1000 THEN PRINT "EXIT THE LIMIT " :STOP
18500 HE=(EH-EL)/10
18550 FOR J7=0 TO 10
18600 ERG=ERG+J7*HE
18650 EG(J7)=ERG
18700 GOSUB 7800 :GOSUB 9750 :GOSUB 8950 :GOSUB 10250
18750 IF I=ITS2 THEN GOSUB 23550 :GOTO 19050
18800 CP=ABS(WN(1)-WN(N))
18850 IF CP<=1E-08 THEN IFLAG=1 :GOTO 20050
18900 ZJ(J7)=CP
18950 PRINT "CP("J7")="ZJ(J7)
19000 GOTO 19250
19050 CC=WN(N1)
19100 IF ABS(CC) < 1E-08 THEN IFLAG=1 :GOTO 20050
19150 ZJ(J7)=ABS(CC)
19200 PRINT "CC("J7")="ZJ(J7)
19250 NEXT J7
19300 CMIN=ZJ(0)
19350 FOR K=1 TO 10
19400 IF ZJ(K) < CMIN THEN CMIN=ZJ(K) :J1=K
19450 NEXT K
19500 PRINT "INC IS="INC
19550 KA=J1-1
19600 KB=J1+1
19650 IF J1=10 THEN EL=EH :EH=EH+TT :INC=INC+1 :GOTO 18400
19700 '
19750 EL=EG(KA)
19800 EH=EG(KB)
19850 IF (EH-EL)<1E-15 THEN PRINT "NEED SMALLER TOLERANCE":STOP
19900 ERG=EL
19950 GOTO 18500
20000 '
20050 RETURN
20100 '
```

```
20150 '@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
20200 '
20250 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
20300 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
20350 '
20400 ' !!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
20450 '
20500 '     THIS SECTION STORES THE NEARLY EXACT WAVE FUNCTIONS
20550 '
20600 '     THE 1'ST EXCITED STATE EIGENVECTOR STORED IN WAVEFCN2 FILE'S
20650 '     THE 2'ND EXCITED STATE EIGENVECTOR STORED IN WAVEFCN3 FILE'S
20700 '     THE 3'TH EXCITED STATE EIGENVECTOR STORED IN WAVEFCN4 FILE'S
20750 '     THE 4'TH EXCITED STATE EIGENVECTOR STORED IN WAVEFCN5 FILE'S
20800 '     THE 5'TH EXCITED STATE EIGENVECTOR STORED IN WAVEFCN6 FILE'S
20850 '     THE 6'TH EXCITED STATE EIGENVECTOR STORED IN WAVEFCN7 FILE'S
20900 '     THE 7'TH EXCITED STATE EIGENVECTOR STORED IN WAVEFCN8 FILE'S
20950 '
21000 OPEN "O",#3,"WAVEFCN2"
21050 FOR K=0 TO NZ+1
21100 PRINT #3,WG(K)
21150 NEXT K
21200 CLOSE #3
21250 RETURN
21300 OPEN "O",#4,"WAVEFCN3"
21350 FOR K=0 TO NZ+1
21400 PRINT #4,WG(K)
21450 NEXT K
21500 CLOSE #4
21550 RETURN
21600 OPEN "O",#5,"WAVEFCN4"
21650 FOR K=0 TO NZ+1
21700 PRINT #5,WG(K)
21750 NEXT K
21800 CLOSE #5
21850 RETURN
21900 OPEN "O",#6,"WAVEFCN5"
21950 FOR K=0 TO NZ+1
22000 PRINT #6,WG(K)
22050 NEXT K
22100 CLOSE #6
22150 RETURN
22200 OPEN "O",#7,"WAVEFCN6"
22250 FOR K=0 TO NZ+1
22300 PRINT #7,WG(K)
22350 NEXT K
22400 RETURN
22450 OPEN "O",#8,"WAVEFCN7"
22500 FOR K=0 TO NZ+1
22550 PRINT #8,WG(K)
22600 NEXT K
22650 CLOSE #8
22700 RETURN
22750 OPEN "O",#9,"WAVEFCN8"
22800 FOR K=0 TO NZ+1
22850 PRINT #9,WG(K)
```

```
22900 NEXT K
22950 CLOSE #9
23000 RETURN
23050 '
23100 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
23150 '
23200 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
23250 '
23300 '    SINCE THE ODD PARITY WAVE-FUNCTION IS ODD FUNCTION THEN
23350 '    , IN ORDER TO COMPARE THE ENTRIES OF THE EIGENVECTOR, WE
23400 '    NEED TO NEGATE THE HALF ENTRIES OF THE EIGEN-VECTOR.
23450 '    THIS PROCESS IS DONE IN THIS SECTION
23500 '
23550 NP1=N+1
23600 NH=NP1/2
23650 FOR K=1 TO NH
23700 WF(NP1-K)=-1*WF(NP1-K)
23750 NEXT K
23800 RETURN
23850 '
23900 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
23950 '*****************************************************************
24000 '
24050 '    THIS SECTION STORE THE NEARLY EXACT EIGEN-ENERGY IN NEWERG
24100 '    FILE.
24150 '
24200 OPEN "O",#10,"NEWERG"
24250 FOR K=1 TO 8
24300 PRINT #10,A(K)
24350 NEXT K
24400 CLOSE #10
24450 RETURN
24500 '
24550 '*****************************************************************
```

APPENDIX C

```
1000 '
1050 '        THIS PROGRAM CALCULATES THE RELATIVE POLARIZABILITIES
1100 '        OF GROUND STATE AND HIGHER STATES OF THE RESTRICTED
1150 '        OSCILLATORS WITH/WITHOUT DIPOLAR INTERACTION.
1200 '
1250 '        THIS PROGRAM IS WRITTEN IN MICROSOFT BASIC AND MUST BE
1300 '        COMPILED IN ORDER TO SPEED UP THE CALCULATION.
1350 '
1400 '        THIS RELATIVE POLARIZABILITY IS DEFINED BY EQUATION (IV:1)
1450 '        IN THE THESIS.
1500 '        WHERE n=0 IS THE GROUND STATE POLARIZABILITY,
1550 '              n=1 IS THE FIRST EXCITED STATE POLARIZABILITY....ETC.
1600 '
1650 '        WE, OF COURSE, USE THE CALCULATED EIGENVALUES AND EIGEN-
1700 '        VECTORS WHICH ARE COMPUTED BY COMPUTER ( REFER TO APPENDIX A
1750 '        AND B) TO CALCULATE THE RELATIVE POLARIZABILITY.
1800 '
1850 '
1900 LPRINT
1950 REM
2000 DEFDBL A,D,H,M,W,Y
2050 DEFSNG B,P
2100 DEFINT I,J,K,N                          :REM  DECLARE INTEGER.
2150 PRINT  "THE NUMBER OF POINT MUST BE AN ODD NUMBER"
2200 INPUT "THE NUMBER OF POINT IS";N        :REM N IS THE NUMBER OF POINT
                                                   BETWEEN THE BOUNDARY POINTS
2250 '
2300 INPUT "THE VALUE OF Y1";Y1              :REM  Y1 IS REFERRED TO -YO
2350 INPUT "THE VALUE OF Y2";Y2              :REM  Y2 IS REFERRED TO +YO
2400 LPRINT
2450 LPRINT "THE NUMBER OF POINT BETWEEN BOUNDARY POINTS IS" N
2500 LPRINT
2550 LPRINT "THE LEFT HAND SIDE LIMIT IS " Y1
2600 LPRINT
2650 LPRINT "THE RIGHT HAND SIDE LIMIT IS " Y2
2700 LPRINT
2750 LPRINT
2800 NZ=N                                    :REM  NZ WILL BE USED LATER.
2850 H=(Y2-1*Y1)/(N+1)                       :REM  H IS LENGTH BETWEEN Yi
2900 HZ=H                                    :'    AND Yi+1.
2950 REM
3000 DIM A(10),MD(10),DP(80),DZ(80),WF(80),WG(80),B(10)
3050 GOSUB 18300
3100 LPRINT
3150 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
3200 '     THIS SECTION CALCULATE THE RELATIVE POLARIZABILITY OF
3250 '     GROUND STATE.
3300 '
3350 GOSUB 13100 : GOSUB 18850
3400 FOR I=2 TO 8
3450 IF I=2 THEN GOSUB 13750
3500 IF I=3 THEN GOSUB 14400
3550 IF I=4 THEN GOSUB 15050
3600 IF I=5 THEN GOSUB 15700
3650 IF I=6 THEN GOSUB 16350
```

```
3700 IF I=7 THEN GOSUB 17000
3750 IF I=8 THEN GOSUB 17650
3800 FOR J=0 TO NZ+1
3850 DP(J)=WG(J)*WF(J)*(Y1+J*HZ)      :REM  CALCULATE THE INTEGRAND OF
3900 DZ(J)=DP(J)                      :REM  DIPOLE MATRIX.
3950 NEXT J
4000 GOSUB 12250
4050 MD(I)=ARE                        :REM  MD(I) IS A MATRIX DIPOLE.
4100 NEXT I
4150 GOSUB 18300
4200 MD(1)=0 :MTX=0
4250 FOR K=2 TO 8                     :REM  MTX IN HERE IS THE RELATIVE
4300 MTX=MTX+(MD(K))^2/(A(K)-A(1))    :'    POLARIZABILITY OF GROUND
4350 NEXT K                           :'    STATE.
4400 P=MTX
4450 LPRINT
4500 LPRINT "THE RELATIVE POLARIZABILITY AT T=0 KELVIN  IS=" P
4550 LPRINT
4600 LPRINT "THE REL POL IN DOUBLE PRECISION IS="MTX
4650 '
4700 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
4750 '
4800 '************************************************************************
4850 '     THIS SECTION CALCULATES THE RELATIVE POLARIZABILITY OF
4900 '     FIRST EXCITED STATE.
4950 '
5000 LPRINT
5050 GOSUB 13750 : GOSUB 18850
5100 FOR I=1 TO 8
5150 IF I=1 THEN GOSUB 13100
5200 IF I=2 THEN I=I+1
5250 IF I=3 THEN GOSUB 14400
5300 IF I=4 THEN GOSUB 15050
5350 IF I=5 THEN GOSUB 15700
5400 IF I=6 THEN GOSUB 16350
5450 IF I=7 THEN GOSUB 17000
5500 IF I=8 THEN GOSUB 17650
5550 FOR J=0 TO NZ+1
5600 DP(J)=WG(J)*WF(J)*(Y1+J*HZ)      :REM  CALCULATE THE INTEGRAND OF
5650 DZ(J)=DP(J)                      :REM  MATRIX DIPOLE.
5700 NEXT J
5750 GOSUB 12250
5800 MD(I)=ARE                        :REM  MD(I) IS A MATRIX DIPOLE.
5850 NEXT I
5900 GOSUB 18300
5950 MD(2)=0 :MTX=0
6000 FOR K=1 TO 8                   :REM  MTX IN HERE IS THE RELATIVE
6050 IF K=2 GOTO 6150               :'    POLARIZABILITY OF THE FIRST
6100 MTX=MTX+(MD(K))^2/(A(K)-A(2))  :'    EXCITED STATE.
6150 NEXT K
6200 P=MTX
6250 LPRINT
6300 LPRINT
6350 LPRINT "RELATIVE POLARIZABILITY OF THE 1'ST EXCITED STATE IS=" P
6400 LPRINT
```

```
6450 LPRINT "THE REL POL OF ABOVE IN DOUBLE PRECISION IS="MTX
6500 LPRINT
6550 '
6600 '****************************************************************
6650 '
6700 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
6750 '     THIS SECTION CALCULATE THE RELATIVE POLARIZABILITY OF
6800 '     SECOND EXCITED STATE.
6850 '
6900 GOSUB 14400 : GOSUB 18850
6950 FOR I=1 TO 8
7000 IF I=1 THEN GOSUB 13100
7050 IF I=2 THEN GOSUB 13750
7100 IF I=3 THEN I=I+1
7150 IF I=4 THEN GOSUB 15050
7200 IF I=5 THEN GOSUB 15700
7250 IF I=6 THEN GOSUB 16350
7300 IF I=7 THEN GOSUB 17000
7350 IF I=8 THEN GOSUB 17650
7400 FOR J=0 TO NZ+1                    :REM  THIS LOOP CALCULATE THE
7450 DP(J)=WG(J)*WF(J)*(Y1+J*HZ)        :REM  INTEGRAND OF DIPOLE MATRIX.
7500 DZ(J)=DP(J)
7550 NEXT J
7600 GOSUB 12250
7650 MD(I)=ARE                          :REM  MD(I) IS THE DIPOLE MATRIX.
7700 NEXT I
7750 GOSUB 18300
7800 MD(3)=0 :MTX=0
7850 FOR K=1 TO 8                       :REM  MTX IN HERE IS THE RELATIVE
7900 IF K=3 GOTO 8000                   :'    POLARIZABILITY OF THE SECOND
7950 MTX=MTX+(MD(K))^2/(A(K)-A(3))      :'    EXCITED STATE.
8000 NEXT K
8050 P=MTX
8100 LPRINT
8150 LPRINT "RELATIVE POLARIZABILITY OF THE 2'ND EXCITED STATE IS=" P
8200 LPRINT
8250 LPRINT "THE REL POL OF ABOVE IN DOUBLE PRECISION IS="MTX
8300 LPRINT
8350 '
8400 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
8450 '
8500 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
8550 '     THIS SECTION CALCULATE THE RELATIVE POLARIZABILITY OF
8600 '     THIRD EXCITED STATE.
8650 '
8700 GOSUB 15050 : GOSUB 18850
8750 FOR I=1 TO 8
8800 IF I=1 THEN GOSUB 13100
8850 IF I=2 THEN GOSUB 13750
8900 IF I=3 THEN GOSUB 14400
8950 IF I=4 THEN I=I+1
9000 IF I=5 THEN GOSUB 15700
9050 IF I=6 THEN GOSUB 16350
9100 IF I=7 THEN GOSUB 17000
9150 IF I=8 THEN GOSUB 17650
```

```
9200 FOR J=0 TO NZ+1                     :REM  THIS LOOP CALCULATES THE
9250 DP(J)=WG(J)*WF(J)*(Y1+J*HZ)         :'    INTEGRAND OF DIPOLE MATRIX.
9300 DZ(J)=DP(J)
9350 NEXT J
9400 GOSUB 12250
9450 MD(I)=ARE                           :REM  MD(I) IS THE DIPOLE MATRIX.
9500 NEXT I
9550 GOSUB 18300
9600 MD(4)=0 :MTX=0
9650 FOR K=1 TO 8                        :REM  MTX IN HERE IS THE RELATIVE
9700 IF K=4 GOTO 9800                    :'    POLARIZABILITY OF THIRD
9750 MTX=MTX+(MD(K))^2/(A(K)-A(4))       :'    EXCITED STATE.
9800 NEXT K
9850 P=MTX
9900 LPRINT
9950 LPRINT "RELATIVE POLARIZABILITY OF THE 3'RD EXCITED STATE IS=" P
10000 LPRINT
10050 LPRINT "THE REL POL OF ABOVE IN DOUBLE PRECISION IS="MTX
10100 '
10150 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
10200 '
10250 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
10300 '     THIS SECTION CALCULATE THE RELATIVE POLARIZABILITY OF
10350 '     FOURTH EXCITED STATE.
10400 '
10450 GOSUB 15700 : GOSUB 18850
10500 FOR I=1 TO 8
10550 IF I=1 THEN GOSUB 13100
10600 IF I=2 THEN GOSUB 13750
10650 IF I=3 THEN GOSUB 14400
10700 IF I=4 THEN GOSUB 15050
10750 IF I=5 THEN I=I+1
10800 IF I=6 THEN GOSUB 16350
10850 IF I=7 THEN GOSUB 17000
10900 IF I=8 THEN GOSUB 17650
10950 FOR J=0 TO NZ+1                   :REM  THIS LOOP CALCULATE THE
11000 DP(J)=WG(J)*WF(J)*(Y1+J*HZ)       :'    INTEGRAND OF DIPOLE MATRIX.
11050 DZ(J)=DP(J)
11100 NEXT J
11150 GOSUB 12250
11200 MD(I)=ARE                         :REM  MD(I) IS THE DIPOLE MATRIX.
11250 NEXT I
11300 GOSUB 18300
11350 MD(5)=0 :MTX=0
11400 FOR K=1 TO 8                      :REM  MTX IN HERE IS THE RELATIVE
11450 IF K=5 GOTO 11550                 :'    POLARIZABILITY OF FOURTH
11500 MTX=MTX+(MD(K))^2/(A(K)-A(5))     :'    EXCITED STATE.
11550 NEXT K
11600 P=MTX
11650 LPRINT
11700 LPRINT "RELATIVE POLARIZABILITY OF THE 4'TH EXCITED STATE IS=" P
11750 LPRINT
11800 LPRINT "THE REL POL OF ABOVE IN DOUBLE PRECISION IS="MTX
11850 '
11900 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
```

```
11950 END
12000 REM
12050 '
12100 '*****************************************************************
12150 '       THIS SECTION CALCULATE THE INTEGRAL USING SIMPSON'S RULE.
12200 '
12250 K=1
12300 AR=DZ(0)+DZ(NZ+1)+4*DZ(K)        :REM  DZ(I) IS THE INTEGRAND
12350 NN=(NZ+1)/2                       :'     AT POINT Yi.
12400 FOR K=2 TO NN
12450 KZ=2*K
12500 ARH=4*DZ(KZ-1)+2*DZ(KZ-2)
12550 AR=AR+ARH
12600 NEXT K
12650 ARE=(HZ/3)*AR
12700 RETURN
12750 '
12800 '****************************************************************
12850 '
12900 '§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§
12950 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE GROUND
13000 '       STATE EIGEN-VECTOR.
13050 '
13100 OPEN "I",#2,"WAVEFCN1"
13150 FOR K=0 TO NZ+1
13200 INPUT #2,WG(K)
13250 NEXT K
13300 CLOSE #2
13350 RETURN
13400 '
13450 '§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§§
13500 '
13550 '*****************************************************************
13600 '     THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE FIRST
13650 '     EXCITED STATE EIGEN-VECTOR.
13700 '
13750 OPEN "I",#3,"WAVEFCN2"
13800 FOR K=0 TO NZ+1
13850 INPUT #3,WG(K)
13900 NEXT K
13950 CLOSE #3
14000 RETURN
14050 '
14100 '****************************************************************
14150 '
14200 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
14250 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE SECOND
14300 '       EXCITED STATE EIGEN-VECTOR.
14350 '
14400 OPEN "I",#4,"WAVEFCN3"
14450 FOR K=0 TO NZ+1
14500 INPUT #4,WG(K)
14550 NEXT K
14600 CLOSE #4
14650 RETURN
```

```
14700 '
14750 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
14800 '
14850 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
14900 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE THIRD
14950 '       EXCITED STATE EIGEN-VECTOR.
15000 '
15050 OPEN "I",#5,"WAVEFCN4"
15100 FOR K=0 TO NZ+1
15150 INPUT #5,WG(K)
15200 NEXT K
15250 CLOSE #5
15300 RETURN
15350 '
15400 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
15450 '
15500 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
15550 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE FOURTH
15600 '       EXCITED STATE EIGEN-VECTOR.
15650 '
15700 OPEN "I",#6,"WAVEFCN5"
15750 FOR K=0 TO NZ+1
15800 INPUT #6,WG(K)
15850 NEXT K
15900 CLOSE #6
15950 RETURN
16000 '
16050 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
16100 '
16150 '**************************************************************
16200 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE FIFTH
16250 '       EXCITED STATE EIGEN-VECTOR.
16300 '
16350 OPEN "I",#7,"WAVEFCN6"
16400 FOR K=0 TO NZ+1
16450 INPUT #7,WG(K)
16500 NEXT K
16550 CLOSE #7
16600 RETURN
16650 '
16700 '**************************************************************
16750 '
16800 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
16850 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE SIXTH
16900 '       EXCITED STATE EIGEN-VECTOR.
16950 '
17000 OPEN "I",#8,"WAVEFCN7"
17050 FOR K=0 TO NZ+1
17100 INPUT #8,WG(K)
17150 NEXT K
17200 CLOSE #8
17250 RETURN
17300 '
17350 '!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
17400 '
```

```
17450 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
17500 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE SEVENTH
17550 '       EXCITED STATE EIGEN-VECTOR.
17600 '
17650 OPEN "I",#9,"WAVEFCN8"
17700 FOR K=0 TO NZ+1
17750 INPUT #9,WG(K)
17800 NEXT K
17850 CLOSE #9
17900 RETURN
17950 '
18000 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
18050 '
18100 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
18150 '       THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE
18200 '       CALCULATED EIGEN-ENERGIES.
18250 '
18300 OPEN "I",#10,"NEWERG"
18350 FOR K=1 TO 8
18400 INPUT #10,A(K)
18450 NEXT K
18500 CLOSE #10
18550 RETURN
18600 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
18650 '
18700 '@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
18750 '      THIS SECTION ASSIGNS WF(K)=WG(K) for k=0 to n+1 {EIGEN
18800 '                                                     -VECTOR}.
18850 FOR K=0 TO NZ+1
18900 WF(K)=WG(K)
18950 NEXT K
19000 RETURN
19050 '@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
```

APPENDIX D

```
1000 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
1050 '      THIS PROGRAM IS WRITTEN IN MICROSOFT BASIC FOR NORTH STAR
1100 '      HORIZON COMPUTER, THIS PROGRAM RUN IN COMPILED BASIC.
1150 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
1200 '
1250 '       PURPOSE : TO CHECK THE COMPUTED EIGEN-ENERGY
1300 '                 AND EIGEN FUNCTION ARE CORRECT OR NOT ( WITHIN
1350 '                 THE LIMIT ).
1400 '
1450 '
1500 '
1550 DEFDBL A,B,E,Y,W,D,H,Z
1600 DEFINT I,J,K,N                         :REM  DECLARE INTEGER.
1650 REM
1700 PRINT "THE NUMBER OF POINT MUST BE AN ODD NUMBER"
1750 PRINT
1800 INPUT "THE NUMBER OF POINT IS";N  :REM N IS THE NUMBER OF POINT
                                              BETWEEN THE BOUNDARY POINTS
1850 INPUT "THE VALUE OF Y1";Y1
1900 INPUT "THE VALUE OF Y2";Y2
1950 PRINT "IF THE SYSTEM IS A RESTRICTED OSCILLATOR ONLY THEN THE"
2000 PRINT "SYSTEM IS INDEPENDENT OF ANGULAR FREQUENCY"
2050 PRINT
2100 INPUT "THE ANGULAR FREQUENCY IS";WO
2150 PRINT
2200 PRINT "THE NUMBER OF POINT BETWEEN BOUNDARY POINTS IS" N
2250 PRINT
2300 PRINT "THE LEFT HAND SIDE LIMIT IS =" Y1
2350 PRINT
2400 PRINT "THE RIGHT HAND SIDE LIMIT IS =" Y2
2450 PRINT
2500 PRINT "THE ANGULAR FREQUENCY IS";WO
2550 PRINT
2600 ' DEF FNV(Y)=(.5*Y)^2                    :REM  POTENTIAL ENERGY FUNCTION.
2650 DEF FNV(Y)=(Y/2)^2*(1-(903355060#/((Y2^3)*(WO^.5))))
2700 ' IF THE SYSTEM IS RESTRICTED OSCILLATOR WITHOUT DIPOLAR INTERACTION
2750 ' THEN #2600 SHOULD BE ACTIVATED ELSE #2650 SHOULD BE ACTIVATED.
2800 '
2850 NZ=N                                  :REM  NZ WILL BE USED LATER.
2900 H=(Y2-1*Y1)/(N+1)                     :REM  H IS LENGTH BETWEEN Yi AND Yi+1.
2950 REM
3000 DIM A(80),WF(80),E(10),Z(80)
3050 '
3100 REM      MATRIX [A] IS A TRIDIAGONAL MATRIX,THEN WE CAN USE 3 VECTORS FOR
              REPRESENTING MATRIX [A].
3150 REM
3200 FOR I=1 TO N                          :REM  THIS LOOP IS USED TO FIND
3250 Y=Y1+I*H                              :REM  THE VALUES OF Yi AND THE
3300 VY=FNV(Y)                             :REM  ENTRIES OF Aii.
3350 A(I)=2/(H^2)+VY
3400 NEXT I
3450 B=-1/(H^2)                         :REM  Bi IS THE SUBDIAGONAL OF [A].
3500 GOSUB 9200
3550 FOR I=1 TO 8
3600 IF I=1 THEN GOSUB 5600
```

```
3650 IF I=2 THEN GOSUB 6250
3700 IF I=3 THEN GOSUB 6900
3750 IF I=4 THEN GOSUB 7550
3800 IF I=5 THEN GOSUB 7950
3850 IF I=6 THEN GOSUB 8250
3900 IF I=7 THEN GOSUB 8550
3950 IF I=8 THEN GOSUB 8850
4000 '
4050 ':::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
4100 '     IN THIS SECTION, WE FIRST MULTIPLY THE MATRIX A WITH
4150 '     VECTOR WF. THIS YIELDS A VECTOR Z. ( [Aij]*WFj = Zj )
4200 '     NOW, DIVIDE THE VECTOR Z WITH SOME COMMON NUMBER,
4250 '     IN HERE, WE CHOOSE ENERGY E(I), WE GET A NEW VECTOR Z.
4300 '     BY COMPARING THIS VECTOR WITH EIGEN-VECTOR, AND IF THE
4350 '     DIFFERENT (DFR) IS A SMALL NUMBER THEN THE EIGEN-VECTOR
4400 '     WF AND EIGEN-ENERGY E CAN BE THOUGHT AS A NEARLY EXACT
4450 '     SOLUTION OF THIS EIGENVALUE PROBLEM.
4500 '
4550 Z(0)=0
4600 Z(1)=A(1)*WF(1)+B*WF(2)
4650 FOR J=2 TO N-1
4700 Z(J)=B*WF(J-1)+A(J)*WF(J)+B*WF(J+1)
4750 NEXT J
4800 Z(N)=B*WF(N-1)+A(N)*WF(N)
4850 Z(N+1)=0
4900 FOR J=0 TO N+1
4950 Z(J)=Z(J)/E(I)   :REM  DIVIDE EACH ENTRY OF VECTOR Z BY A NUMBER,
                            FOR CONVENIIENT, WE CHOOSE ENERGY E(I).
5000 DFR=ABS(Z(J)-WF(J))
5050 IF DFR > .00001 THEN PRINT "THE DIFFERENCE OF ITS COORDINATE IS";DFR
                     ELSE PRINT "Z("J")-WF("J")=";DFR
5100 NEXT J
5150 '
5200 '::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
5250 NEXT I
5300 END
5350 '
5400 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
5450 '     THIS SECTION ACCESSES THE FILES WHICH CONTAINS THE
5500 '     GROUND STATE EIGEN-VECTOR.
5550 '
5600 OPEN "I",#2,"WAVEFCN1"
5650 FOR K=0 TO NZ+1
5700 INPUT #2,WF(K)
5750 NEXT K
5800 CLOSE #2
5850 RETURN
5900 '
5950 '$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
6000 '
6050 '***************************************************************
6100 '     THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE
6150 '     FIRST EXCITED STATE EIGEN-VECTOR.
6200 '
6250 OPEN "I",#3,"WAVEFCN2"
```

```
6300 FOR K=0 TO NZ+1
6350 INPUT #3,WF(K)
6400 NEXT K
6450 CLOSE #3
6500 RETURN
6550 '
6600 '**************************************************************
6650 '
6700 '@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
6750 '     THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE
6800 '     SECOND EXCITED STATE EIGEN-VECTOR.
6850 '
6900 OPEN "I",#4,"WAVEFCN3"
6950 FOR K=0 TO NZ+1
7000 INPUT #4,WF(K)
7050 NEXT K
7100 CLOSE #4
7150 RETURN
7200 '
7250 '@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@@
7300 '
7350 '################################################################
7400 '     THIS SECTION ACCESSES THE FILE WHICH CONTAINS THE
7450 '     THIRD EXCITED STATE EIGEN-VECTOR.
7500 '
7550 OPEN "I",#5,"WAVEFCN4"
7600 FOR K=0 TO NZ+1
7650 INPUT #5,WF(K)
7700 NEXT K
7750 CLOSE #5
7800 RETURN
7850 '
7900 '################################################################
7950 OPEN "I",#6,"WAVEFCN5"
8000 FOR K=0 TO NZ+1
8050 INPUT #6,WF(K)
8100 NEXT K
8150 CLOSE #6
8200 RETURN
8250 OPEN "I",#7,"WAVEFCN6"
8300 FOR K=0 TO NZ+1
8350 INPUT #7,WF(K)
8400 NEXT K
8450 CLOSE #7
8500 RETURN
8550 OPEN "I",#8,"WAVEFCN7"
8600 FOR K=0 TO NZ+1
8650 INPUT #8,WF(K)
8700 NEXT K
8750 CLOSE #8
8800 RETURN
8850 OPEN "I",#9,"WAVEFCN8"
8900 FOR K=0 TO NZ+1
8950 INPUT #9,WF(K)
9000 NEXT K
```

```
9050 CLOSE #9
9100 RETURN
9150 '
9200 OPEN "I",#10,"NEWERG"
9250 FOR K=1 TO 8
9300 INPUT #10,E(K)
9350 NEXT K
9400 CLOSE #10
9450 RETURN
```