Complementary bounds for dynamic polarizabilities

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Complementary bounds for dynamic polarizabilities

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Abstract. Complementary variational principles are developed for ground-state wave function corrections which are induced by frequency-dependent perturbations. These principles lead to upper and lower bounds for dynamic polarizabilities which are either measured at real frequencies less in magnitude than the first excitation energy, or measured at any imaginary frequencies. In the latter case there is a choice of upper bounds, different forms being suited to small and large frequencies. Illustrative results are presented for the hydrogen atom, and reasonable accuracy is obtained with simple one-parameter trial functions.

1. Introduction

In a recent paper (Robinson 1969), complementary variational principles associated with the first-order correction

$$(h-\mathscr{E})\Phi = (\bar{V}-V)\psi_0 \tag{1}$$

to the ground-state wave equation

$$(h-\epsilon_0)\psi_0 = 0 \tag{2}$$

were discussed. Here h is a Hamiltonian with orthonormal eigenfunctions $\{\psi_n\}$ and energy eigenvalues $\{\epsilon_n\}$, V is a perturbation and

$$\bar{V} = \int \psi_0 V \psi_0 \,\mathrm{d}\boldsymbol{r} = (\psi_0, V\psi_0). \tag{3}$$

The principles led to complementary upper and lower bounds for the second-order energy correction

$$E_{(2)} = \int \phi\{V-\bar{V}\}\psi_0 \,\mathrm{d}\boldsymbol{r} = (\phi, \{V-\bar{V}\}\psi_0) \tag{4}$$

the closeness of these bounds measuring the accuracy of approximations to the exact solution $\Phi = \phi$ of (1). When $\mathscr{E} = \epsilon_0$ the results refer to conventional Rayleigh–Schrödinger perurbation theory; otherwise they refer to Brillouin–Wigner theory.

In the present paper these ideas are extended to yield complementary upper and lower bounds for dynamic polarizabilities at both real and imaginary frequencies. Accuracy of appropriate first-order wave functions can also be tested. Real frequencies can be dealt with by setting $\mathscr{E} = \epsilon_0 + \omega$ in equation (1), but for imaginary frequencies the basic theory must be modified. Illustrative results are presented for the hydrogen atom, and reasonable accuracy is achieved with simple trial functions involving single multiplicative parameters.

A knowledge of dynamic polarizabilities enables one to determine such quantities as refractive index when the frequencies are real (Chan and Dalgarno 1965) and van der Waals coefficients when the frequencies are imaginary (Mavroyannis and Stephen 1962).

2. Basic theory

Following the theory of the earlier paper (Robinson 1969), complementary upper and lower bounds

$$G(\Phi_1) \geqslant S(\phi) \geqslant J(T\Phi_2) \tag{5}$$

are available for the functional

$$S(\phi) = -\tfrac{1}{2}\int \phi f \,\mathrm{d}\boldsymbol{r} \tag{6}$$

associated with the exact solution $\Phi = \phi$ of the equation

$$(T^{\dagger}T+Q)\Phi = f. \tag{7}$$

Here T is a linear operator, $T^{\dagger}$ is its adjoint defined by

$$\int (T^{\dagger}U)\Phi \, d\mathbf{r} = \int U(T\Phi) \, d\mathbf{r} \tag{8}$$

Q is a self-adjoint positive-definite operator with an inverse and f is a function of co-ordinates. The expressions for the functionals G and J (which are stationary at $S(\phi)$) are

$$G(\Phi_1) = -\tfrac{1}{2}\int \{-\Phi_1(T^{\dagger}T+Q)\Phi_1+2\Phi_1 f\} \, d\mathbf{r} \tag{9}$$

and

$$J(T\Phi_2) = G(\Phi_2)-\tfrac{1}{2}\int \{f-(T^{\dagger}T+Q)\Phi_2\}Q^{-1}\{f-(T^{\dagger}T+Q)\Phi_2\} \, d\mathbf{r}. \tag{10}$$

So far we have supposed that all functions are real. It is easy to adjust the functionals S, G and J to allow for complex Φ and f provided that $T^{\dagger}T$ and Q remain real. We replace Φf by $\frac{1}{2}(\Phi^* f+\Phi f^*)$, $\Phi_1(T^{\dagger}T+Q)\Phi_1$ by $\Phi_1^*(T^{\dagger}T+Q)\Phi_1$ and the first bracket in (10) by $\{f^*-(T^{\dagger}T+Q)\Phi_2^*\}$. This can be seen by adding the functionals obtained for the real and imaginary parts of equation (7) taken separately; alternatively the basic theory can be adapted using complex scalar products. However, the situation is more difficult if Q is complex, as we see below.

3. Extension of theory for a complex operator

In order to obtain complementary bounds for polarizabilities at imaginary frequencies, we need to consider a modification of the basic equation (7). The simplest suitable one is

$$(\mathcal{T}^{\dagger}\mathcal{T}+a+ib)\Phi = g, \qquad a > 0 \tag{11}$$

where g is real and a and b are real constants. The solution $\Phi = \phi$ of (11) is complex and the bounds (5) do not hold since $a+ib$ is not an acceptable choice for Q.

To make progress we consider the equation

$$\{(\mathcal{T}^{\dagger}\mathcal{T}+a)^2+b^2\}\Theta = g, \qquad (\Theta \text{ real}) \tag{12}$$

with solution $\Theta = \theta$. From (11) and (12) it follows that

$$\Phi = (\mathcal{T}^{\dagger}\mathcal{T}+a-ib)\Theta \tag{13}$$

$$\Phi^* = (\mathcal{T}^{\dagger}\mathcal{T}+a+ib)\Theta \tag{14}$$

and

$$\tfrac{1}{2}(\Phi^*+\Phi) = (\mathcal{T}^{\dagger}\mathcal{T}+a)\Theta. \tag{15}$$

It is possible to treat (12) as an example of (7); but this would provide bounds for $\int\theta g \, d\mathbf{r}$, which is not of interest. Instead we operate on (12) with $(\mathcal{T}^{\dagger}\mathcal{T}+a)$, obtaining

$$\{(\mathcal{T}^{\dagger}\mathcal{T}+a)^3+b^2(\mathcal{T}^{\dagger}\mathcal{T}+a)\}\Theta = (\mathcal{T}^{\dagger}\mathcal{T}+a)g \tag{16}$$

and treat (16) as an example of (7) with

$$T^{\dagger}T+Q = (\mathcal{T}^{\dagger}\mathcal{T}+a)\{(\mathcal{T}^{\dagger}\mathcal{T})^2+2a(\mathcal{T}^{\dagger}\mathcal{T})+a^2+b^2\} \tag{17}$$

and

$$f = (\mathcal{T}^{\dagger}\mathcal{T}+a)g. \tag{18}$$

This procedure yields bounds for the functional

$$\mathcal{S}(\theta) = -\tfrac{1}{2}\int \theta(\mathcal{T}^{\dagger}\mathcal{T}+a)g \, d\mathbf{r} = -\tfrac{1}{2}\int g(\mathcal{T}^{\dagger}\mathcal{T}+a)\theta \, d\mathbf{r} = -\tfrac{1}{4}\int (\phi^*+\phi)g \, d\mathbf{r} \tag{19}$$

from (15). These are

$$\mathcal{G}(\Theta_1) \geqslant \mathcal{S}(\theta) \geqslant \mathcal{J}(\mathcal{T}\Theta_2) \tag{20}$$

where

$$\mathcal{G}(\Theta_1) = -\tfrac{1}{2}\int [-\Theta_1(\mathcal{T}^\dagger\mathcal{T}+a)\{(\mathcal{T}^\dagger\mathcal{T}+a)^2+b^2\}\Theta_1+2\{(\mathcal{T}^\dagger\mathcal{T}+a)\Theta_1\}g]\,\mathrm{d}\boldsymbol{r} \tag{21}$$

and

$$\begin{aligned}\mathcal{J}(\mathcal{T}\Theta_2) = {} & \mathcal{G}(\Theta_2)\\ & -\tfrac{1}{2}\int [g-\{(\mathcal{T}^\dagger\mathcal{T}+a)^2+b^2\}\Theta_2](\mathcal{T}^\dagger\mathcal{T}+a)Q^{-1}(\mathcal{T}^\dagger\mathcal{T}+a)\\ & \times[g-\{(\mathcal{T}^\dagger\mathcal{T}+a)^2+b^2\}\Theta_2]\,\mathrm{d}\boldsymbol{r}.\end{aligned} \tag{22}$$

If functions Φ_1 and Φ_2 are given in terms of Θ_1 and Θ_2 according to equations (13)–(15), these expressions can be written in the alternative forms

$$\mathcal{G} = -\tfrac{1}{2}\int \{-\Phi_1^*(\mathcal{T}^\dagger\mathcal{T}+a)\Phi_1+(\Phi_1^*+\Phi_1)g\}\,\mathrm{d}\boldsymbol{r} \tag{23}$$

and

$$\begin{aligned}\mathcal{J} = {} & \mathcal{G}\\ & -\tfrac{1}{2}\int \{g-(\mathcal{T}^\dagger\mathcal{T}+a-\mathrm{i}b)\Phi_2^*\}(\mathcal{T}^\dagger+a)Q^{-1}(\mathcal{T}^\dagger\mathcal{T}+a)\{g-(\mathcal{T}^\dagger\mathcal{T}+a+\mathrm{i}b)\Phi_2\}\,\mathrm{d}\boldsymbol{r}.\end{aligned} \tag{24}$$

The upper bound $\mathcal{G}$ is independent of the way in which T and Q are chosen to satisfy (17), but the lower bound $\mathcal{J}$ will be maximized if Q is made as 'large' as possible. In principle we could choose for example

$$T^\dagger T = (\mathcal{T}^\dagger\mathcal{T})^3, \qquad Q = 3a(\mathcal{T}^\dagger\mathcal{T})^2+(3a^2+b^2)\mathcal{T}^\dagger\mathcal{T}+a(a^2+b^2) \tag{25}$$

but then Q^{-1} is clumsy so that the evaluation of (24) is not practicable. More sensible choices are

$$T^\dagger T = \mathcal{T}^\dagger\mathcal{T}(\mathcal{T}^\dagger\mathcal{T}+a)^2+b^2(\mathcal{T}^\dagger\mathcal{T}+a), \qquad Q = a(\mathcal{T}^\dagger\mathcal{T}+a)^2 \tag{26}$$

leading to

$$\mathcal{J}_{\mathrm{I}} = \mathcal{G}-\frac{1}{2a}\int \{g-(\mathcal{T}^\dagger\mathcal{T}+a-\mathrm{i}b)\Phi_2^*\}\{g-(\mathcal{T}^\dagger\mathcal{T}+a+\mathrm{i}b)\Phi_2\}\,\mathrm{d}\boldsymbol{r} \tag{27}$$

or

$$T^\dagger T = \mathcal{T}^\dagger\mathcal{T}(\mathcal{T}^\dagger\mathcal{T}+a)(\mathcal{T}^\dagger\mathcal{T}+2a), \qquad Q = (a^2+b^2)(\mathcal{T}^\dagger\mathcal{T}+a) \tag{28}$$

leading to

$$\mathcal{J}_{\mathrm{II}} = \mathcal{G}-\frac{1}{2(a^2+b^2)}\int \{g-(\mathcal{T}^\dagger\mathcal{T}+a-\mathrm{i}b)\Phi_2^*\}(\mathcal{T}^\dagger\mathcal{T}+a)\{g-(\mathcal{T}^\dagger\mathcal{T}+a+\mathrm{i}b)\Phi_2\}\,\mathrm{d}\boldsymbol{r}. \tag{29}$$

In the case $b = 0$, equation (11) is a direct example of (7) with

$$\mathcal{T} = T, \qquad Q = a, \qquad g = f, \qquad \Phi \text{ real.} \tag{30}$$

Denoting the functionals for zero b by $\mathcal{S}_0$, $\mathcal{G}_0$, $\mathcal{J}_0$, it is evident from (6), (9), (10), (19), (23) and (27) that

$$\mathcal{S} \to \mathcal{S}_0,\ \mathcal{G} \to \mathcal{G}_0,\ \mathcal{J}_{\mathrm{I}} \to \mathcal{J}_0 \qquad \text{as } b \to 0. \tag{31}$$

Thus we expect $\mathcal{J}_{\mathrm{I}}$ to be a suitable lower bound when b is small. When b is large, $\mathcal{J}_{\mathrm{II}}$ seems suitable by virtue of the factor $(a^2+b^2)^{-1}$.

4. Dynamic polarizabilities at real frequencies

When a system in state ψ_0 is perturbed by the dipole moment operator

$$V(\mathrm{e}^{\mathrm{i}\omega t}+\mathrm{e}^{-\mathrm{i}\omega t}) \tag{32}$$

the polarizability $\alpha(\omega)$ at real positive frequency ω can be defined as

$$\alpha(\omega) = \sum_{n\neq 0} \left(\frac{1}{\epsilon_n-\epsilon_0+\omega}+\frac{1}{\epsilon_n-\epsilon_0-\omega}\right)(\psi_0, V\psi_n)(\psi_n, V\psi_0). \tag{33}$$

If $\phi^{\pm}$ are the solutions for $\Phi^{\pm}$ of the equations

$$(h-\epsilon_0\pm\omega)\Phi^{\pm} = (\bar{V}-V)\psi_0 \tag{34}$$

then we may sum the series (33) and obtain

$$\alpha(\omega) = \alpha^{+}(\omega)+\alpha^{-}(\omega) \tag{35}$$

where

$$\alpha^{\pm}(\omega) = \int \phi^{\pm}(\bar{V}-V)\psi_0\,\mathrm{d}\boldsymbol{r}. \tag{36}$$

The functions $\phi^{\pm}$ are closely related to the first-order corrections to ψ_0 (see (48)–(50) below). It is convenient to introduce the term $\bar{V}$ into (34), for since

$$(\psi_0, (\bar{V}-V)\psi_0) = 0 \tag{37}$$

the orthogonality

$$(\psi_0, \phi^{\pm}) = 0 \tag{38}$$

follows. Thus equation (34) can be regarded as being on D_0, the domain of functions orthogonal to ψ_0. If ϵ_1 is the first excited energy of h, then $h-\epsilon_1$ is a positive-definite, self-adjoint operator on D_0, and so for some T we can write

$$h-\epsilon_1 = T^{\dagger}T \tag{39}$$

(Mikhlin 1964). It should be noted that the term $\bar{V}$ is redundant in (36), since $\phi^{\pm}\in D_0$.

We complete the identification of equations (34) and (7) by setting

$$\epsilon_1-\epsilon_0\pm\omega = Q \tag{40}$$

$$(\bar{V}-V)\psi_0 = f. \tag{41}$$

Then provided that

$$\epsilon_1-\epsilon_0\pm\omega > 0 \tag{42}$$

the basic theory of § 2 leads to complementary upper and lower bounds for

$$S(\phi^{\pm}) = -\tfrac{1}{2}\alpha^{\pm}(\omega). \tag{43}$$

Since ω is non-negative, we always get bounds for $\frac{1}{2}\alpha^{+}(\omega)$. But there will only be unconditional bounds of this nature for $\frac{1}{2}\alpha^{-}(\omega)$, and hence for the polarizability $\alpha(\omega)$ itself, if

$$\epsilon_1-\epsilon_0 > \omega \tag{44}$$

so that Q is positive. The final result is

$$-2G^{+}(\Phi_1{}^{+})-2G^{-}(\Phi_1{}^{-}) \leqslant \alpha(\omega) \leqslant -2J^{+}(T\Phi_2{}^{+})-2J^{-}(T\Phi_2{}^{-}) \tag{45}$$

where

$$2G^{\pm}(\Phi) = \int \{\Phi(h-\epsilon_0\pm\omega)\Phi-2\Phi(\bar{V}-V)\psi_0\}\,\mathrm{d}\boldsymbol{r} \tag{46}$$

and

$$2J^{\pm}(T\Phi) = 2G^{\pm}(\Phi)-(\epsilon_1-\epsilon_0\pm\omega)^{-1}\int\{(\bar{V}-V)\psi_0-(h-\epsilon_0\pm\omega)\Phi\}^2\,\mathrm{d}\boldsymbol{r}. \tag{47}$$

The term $\bar{V}$ is redundant in (46) since $\Phi\in D_0$.

Each functional can be individually optimized with respect to the choice of Φ. Also the closeness of the pairs (G^{+}, J^{+}) and (G^{-}, J^{-}) measures the accuracy of $\Phi^{\pm}$ as approximations to the solutions $\phi^{\pm}$ of (34) when the same $\Phi^{\pm}$ is used in each pair. The first-order correction to the wave function $\psi_0\exp(-\mathrm{i}\epsilon_0 t)$ induced by the perturbation (32) is in fact

$$\phi^{+\prime}\,\mathrm{e}^{\mathrm{i}\omega t}+\phi^{-\prime}\,\mathrm{e}^{-\mathrm{i}\omega t} \tag{48}$$

where

$$(h-\epsilon_0 \pm \omega)\phi^{\pm\prime} = -V\psi_0 \tag{49}$$

(Hirschfelder *et al.* 1964), so that from (34) and (49) it follows that

$$\phi^{\pm\prime} = \phi^{\pm} \mp \frac{1}{\omega}\bar{V}\psi_0, \qquad \omega \neq 0. \tag{50}$$

5. Dynamic polarizabilities at imaginary frequencies

If ω is replaced by $\mathrm{i}\omega$ in equations (32)–(36), we obtain corresponding expressions for the polarizability $\alpha(\mathrm{i}\omega)$ at imaginary frequency ω. We can identify

$$(h-\epsilon_0+\mathrm{i}\omega)\Phi^+ = (\bar{V}-V)\psi_0 \tag{51}$$

with equation (11) if we take

$$h-\epsilon_1 = \mathscr{T}^\dagger\mathscr{T} \qquad \text{(again on } D_0\text{)} \tag{52}$$

$$\epsilon_1-\epsilon_0 = a \tag{53}$$

$$\omega = b \tag{54}$$

$$(\bar{V}-V)\psi_0 = g \tag{55}$$

$$\Phi^+ = \Phi, \qquad \Phi^- = \Phi^*. \tag{56}$$

Then from (19)

$$\mathscr{S}(\theta) = -\tfrac{1}{4}\{\alpha^+(\mathrm{i}\omega)+\alpha^-(\mathrm{i}\omega)\} = -\tfrac{1}{4}\alpha(\mathrm{i}\omega) \tag{57}$$

for which we obtain complementary upper and lower bounds irrespectively of the value of ω. Specifically we have

$$-4\,\mathscr{G} \leqslant \alpha(\mathrm{i}\omega) \leqslant -4\mathscr{J}_{\mathrm{I}} \text{ or } -4\mathscr{J}_{\mathrm{II}} \tag{58}$$

where

$$2\,\mathscr{G} = \int \{\Phi_1{}^*(h-\epsilon_0)\Phi_1-(\Phi_1{}^*+\Phi_1)(\bar{V}-V)\psi_0\}\,\mathrm{d}\boldsymbol{r} \tag{59}$$

and

$$2\mathscr{J}_{\mathrm{I}} = 2\,\mathscr{G}-(\epsilon_1-\epsilon_0)^{-1} \times \int \{(\bar{V}-V)\psi_0-(h-\epsilon_0-\mathrm{i}\omega)\Phi_2{}^*\}\{(\bar{V}-V)\psi_0-(h-\epsilon_0+\mathrm{i}\omega)\Phi_2\}\,\mathrm{d}\boldsymbol{r} \tag{60}$$

or

$$2\mathscr{J}_{\mathrm{II}} = 2\,\mathscr{G}-\{(\epsilon_1-\epsilon_0)^2+\omega^2\}^{-1} \times \int \{(\bar{V}-V)\psi_0-(h-\epsilon_0-\mathrm{i}\omega)\Phi_2{}^*\}(h-\epsilon_0)\{(\bar{V}-V)\psi_0-(h-\epsilon_0+\mathrm{i}\omega)\Phi_2\}\,\mathrm{d}\boldsymbol{r}. \tag{61}$$

We expect $\mathscr{J}_{\mathrm{I}}$ to be more suitable for low frequencies and $\mathscr{J}_{\mathrm{II}}$ for high frequencies.

Should ϵ_1 be unknown, the factor $(\epsilon_1-\epsilon_0)^2$ can be omitted from (61) at the expense of worsening $\mathscr{J}_{\mathrm{II}}$. (If this is done then the restriction $\Phi_2 \in D_0$ can also be dropped.) This weaker result comes directly from the theory of § 3 if we set $a = 0$.

Relations (13) and (14) become

$$\Phi = (h-\epsilon_0-\mathrm{i}\omega)\Theta \tag{62}$$

$$\Phi^* = (h-\epsilon_0+\mathrm{i}\omega)\Theta. \tag{63}$$

These form a constraint on the trial functions Φ_1 and Φ_2, which if not chosen via a trial Θ, must necessarily satisfy

$$\omega(\Phi+\Phi^*) = \mathrm{i}(h-\epsilon_0)(\Phi-\Phi^*). \tag{64}$$

6. Illustrative results for the hydrogen atom

To illustrate the foregoing theory, we suppose that equations (34) and (51) refer to a ground-state hydrogen atom perturbed by an electric field in the z direction, so that

$$h = -\tfrac{1}{2}\nabla^2 - \frac{1}{r}, \qquad \psi_0 = \pi^{-1/2}\,\mathrm{e}^{-r}, \qquad \epsilon_0 = -\tfrac{1}{2}, \qquad \epsilon_1 = -\tfrac{1}{8} \tag{65}$$

and

$$V = -z, \qquad \bar{V} = 0. \tag{66}$$

When $\omega = 0$, the solution of either equation is

$$\phi(0) = (1+\tfrac{1}{2}r)z\psi_0, \qquad (\in D_0) \tag{67}$$

but when $\omega \neq 0$ it is not possible to find a simple form for the exact solutions. At best one can derive complicated expressions for the Laplace transforms of the solutions (cf. Karplus and Kolker 1963), which in turn lead to unwieldy infinite summations for the dynamic polarizabilities. Thus simple variational solutions are of some interest.

6.1. *Real frequencies*, $\omega < \frac{3}{8}$

We see from (44) and (65) that the complementary bounds (45) hold for $\alpha(\omega)$ if

$$\tfrac{3}{8} > \omega\ (\geqslant 0) \tag{68}$$

and so we take as trial functions

$$\Phi_j^{\pm} = A_j^{\pm}\phi(0) \qquad j = 1, 2. \tag{69}$$

Choosing the factors $A_j^{\pm}$ to optimize the respective bounds, we obtain the results

$$A_1^{\pm} = (1 \pm \tfrac{43}{18}\omega)^{-1}, \qquad A_2^{\pm} = (1 \pm \tfrac{3}{2}\omega)^{-1} \tag{70}$$

$$-2G^{\pm} = \tfrac{9}{4}(1 \pm \tfrac{43}{18}\omega)^{-1} \tag{71}$$

$$-2J^{\pm} = \tfrac{3}{14}\{24(3 \pm 8\omega)^{-1} + 5(2 \pm 3\omega)^{-1}\} \tag{72}$$

$$\tfrac{9}{2}\{1-(\tfrac{43}{18}\omega)^2\}^{-1} \leqslant \alpha(\omega) \leqslant \tfrac{6}{7}\{36(9-64\omega^2)^{-1} + 5(4-9\omega^2)^{-1}\}. \tag{73}$$

Examples of (73) are

$$4{\cdot}77 < \alpha(0{\cdot}1) < 4{\cdot}79 \text{ and } 5{\cdot}83 < \alpha(0{\cdot}2) < 5{\cdot}97. \tag{74}$$

For sufficiently small ω, the bounds in (73) differ by $O(\omega^4)$.

6.2. *Imaginary frequencies, small* ω

The solution in D_0 of

$$(h-\epsilon_0)^2\theta(0) = (h-\epsilon_0)\phi(0) = z\psi_0 \tag{75}$$

is

$$\theta(0) = \tfrac{1}{12}(2r^2 + 11r + 22)z\psi_0. \tag{76}$$

Thus, from (62), we use the trial functions

$$\Phi_j = (h-\epsilon_0-\mathrm{i}\omega)\Theta_j, \qquad j = 1, 2 \tag{77}$$

in $\mathscr{G}$ and $\mathscr{J}_{\mathrm{I}}$, where

$$\Theta_j = B_j\theta(0), \qquad j = 1, 2 \tag{78}$$

and we expect to get reasonable results when ω is small. Optimizing, we find that

$$B_1 = (1 + \tfrac{319}{64}\omega^2)^{-1}, \qquad B_2 = \frac{1+\frac{172}{5}\omega^2}{1+\frac{369}{10}\omega^2 + \frac{9673}{45}\omega^4} \tag{79}$$

and

$$-4\,\mathscr{G} \leqslant \alpha(\mathrm{i}\omega) \leqslant -4\mathscr{J}_{\mathrm{I}} \tag{80}$$

where

$$-4\,\mathscr{G} = \tfrac{9}{2}(1+\tfrac{319}{54}\omega^2)^{-1} \tag{81}$$

$$-4\mathscr{J}_{\mathrm{I}} = \tfrac{16}{3} - \frac{\tfrac{5}{6}\{1+\tfrac{172}{5}\omega^2\}^2}{1+\tfrac{369}{10}\omega^2+\tfrac{9673}{45}\omega^4}. \tag{82}$$

The bounds (81) and (82) differ by $O(\omega^4)$.

The upper bound $-4\mathscr{J}_{\mathrm{II}}$ can also be evaluated using a trial function $B_3\theta(0)$, giving optimum values

$$B_3 = (1+\tfrac{576}{47}\omega^2)^{-1} \tag{83}$$

and

$$-4\mathscr{J}_{\mathrm{II}} = \tfrac{9}{68}\{81(1+\tfrac{64}{9}\omega^2)^{-1} - 47(1+\tfrac{576}{47}\omega^2)^{-1}\}. \tag{84}$$

We expect $\mathscr{J}_{\mathrm{I}}$ to be better than $\mathscr{J}_{\mathrm{II}}$ for small ω, although $\mathscr{J}_{\mathrm{II}}$ has the correct limit at $\omega = 0$ since the trial function is exact there. But as ω increases, $\mathscr{J}_{\mathrm{II}}$ should improve at the expense of $\mathscr{J}_{\mathrm{I}}$. This is borne out by the numerical values in table 1.

6.3. *Imaginary frequencies, large* ω

The bounds (81) and (82) are still valid for large ω, but we should not expect too much accuracy as they are based on trial functions which are exact at zero ω. We note that, for large ω,

$$-4\,\mathscr{G} \sim \left(\frac{243}{319}\right)\frac{1}{\omega^2}, \qquad -4\mathscr{J}_{\mathrm{I}} \sim \text{constant}, \qquad -4\mathscr{J}_{\mathrm{II}} \sim \frac{1}{\omega^2} \tag{85}$$

so that the behaviour of $\mathscr{J}_{\mathrm{I}}$ is sadly astray. The correct behaviour is

$$\alpha(\mathrm{i}\omega) \sim \frac{1}{\omega^2} \tag{86}$$

since from (51) we have

$$\phi \sim -\frac{\mathrm{i}}{\omega} z\psi_0, \qquad \phi^* \sim \frac{\mathrm{i}}{\omega} z\psi_0 \tag{87}$$

which yields (86), using (36) and (56). Thus $\mathscr{J}_{\mathrm{II}}$ is still quite good for large ω.

Guided by (87), we hope that the simple trial functions

$$\Theta_j = C_j z\psi_0, \qquad j = 1, 2 \tag{88}$$

will give a better $\mathscr{G}$ and $\mathscr{J}_{\mathrm{II}}$ for large ω. For $\mathscr{G}$ we get the optimum values

$$C_1 = -4\,\mathscr{G}' = (\omega^2+\tfrac{4}{3})^{-1} \tag{89}$$

but for $\mathscr{J}_{\mathrm{II}}$ because of infinite integrals we need to take

$$C_2 = 0 \tag{90}$$

giving the optimum

$$-4\mathscr{J}_{\mathrm{II}}' = (\omega^2+\tfrac{9}{64})^{-1}. \tag{91}$$

From table 2 we see that $\mathscr{G}'$ is better than $\mathscr{G}$ when $\omega \geqslant 2$, but $\mathscr{J}_{\mathrm{II}}'$ is no improvement on $\mathscr{J}_{\mathrm{II}}$. These latter bounds are indeed very close to one another.

The closeness of complementary trial solutions of the various first-order corrections to the wave equation is measured by the difference in the parameter pairs (A_1^+, A_2^+), (A_1^-, A_2^-), (B_1, B_2), (B_1, B_3) and (C_1, C_2). These differences are an order of magnitude greater than the difference in the corresponding complementary bounds, in keeping with the stationary principles. If more accurate solutions are desired, then more than one variable parameter is necessary.

7. Discussion

The stationary property of the G-type functionals is well known; for real frequencies see Karplus and Kolker (1963), Musulin and Epstein (1964), Chan and Dalgarno (1965), and for imaginary frequencies Mavroyannis and Stephen (1962) and Epstein (1968). It

Table 1. Bounds for $\alpha(i\omega)$; $0 \leqslant \omega \leqslant 1$

ω	0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
$-4\mathscr{G}$	4·5	4·249	3·64	2·94	2·31	1·82	1·44	1·16	0·94	0·78	0·65
$-4\mathscr{J}_{I}$	4·5	4·251	3·66	3·03	2·49	2·09	1·79	1·57	1·41	1·29	1·20
$-4\mathscr{J}_{II}$	4·5	4·467	4·17	3·58	2·91	2·33	1·86	1·50	1·12	1·01	0·85

Table 2. Bounds for $\alpha(i\omega)$; $1 \leqslant \omega \leqslant 10$

ω	1·0	2·0	3·0	4·0	5·0	6·0	7·0	8·0	9·0	10·0
$-4\mathscr{G}$	0·65	0·183	0·083	0·0471	0·0303	0·0211	0·0155	0·0119	0·0094	0·0076
$-4\mathscr{G}'$	0·43	0·187	0·097	0·0577	0·0380	0·0268	0·0119	0·0153	0·0121	0·0099
$-4\mathscr{J}_{II}$	0·85	0·240	0·109	0·0618	0·0397	0·0276	0·0203	0·0156	0·0123	0·0100
$-4\mathscr{J}_{II}'$	0·88	0·242	0·109	0·0620	0·0398	0·0277	0·0203	0·0156	0·0123	0·0100

has also been realized that these functionals provide bounds in certain cases. However, the complementary J-type functionals would seem to be new, and the possibility of testing approximate first-order wave functions with pairs of complementary bounds is an additional feature.

Recent work by Goscinski (1968) shows how upper and lower bounds can be obtained for $\alpha(i\omega)$ by operator analysis. He finds bounds in terms of the sums

$$S_{k-1} = 2 \sum_{n \neq 0} (\epsilon_n - \epsilon_0)^k (\psi_0, V\psi_n)(\psi_n, V\psi_0), \qquad -5 \leqslant k \leqslant 3 \tag{92}$$

which are often available from experimental data. One can derive results like Goscinski's by taking as trial functions in $\mathscr{G}$ and $\mathscr{J}$ optimized linear combinations of

$$(h - \epsilon_0)^m V\psi_0 \tag{93}$$

for various values of m. Gordon (1968) has also employed the sums (92) to give bounds for $\alpha(i\omega)$ using Gaussian integration techniques.

An upper bound for $\alpha(i\omega)$ is given by Epstein (1968) in terms of an upper bound for $\alpha(0)$. The writer is grateful to this author for stimulating his interest in dynamic polarizabilities.

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