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PHYSICS OF PLANETARY ATMOSPHERES III:
THE TIME-DEPENDENT COUPLED HARTREE-FOCK APPROXIMATION

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By G. A. Victor and A. Dalgarno

ABSTRACT

A coupled Hartree-Fock approximation for describing the effects of time-dependent perturbations on many-electron systems is presented. It is applied to the calculation of the frequency-dependent refractive index of helium gas with results that differ by between 4% and 8% from the accurate values obtained by a refined variational calculation.

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INTRODUCTION

There are two general schemes of approximation in the time-independent theory of many electron systems, the uncoupled and the coupled Hartree-Fock approximations [1]*. Time-dependent Hartree-Fock equations were derived by Dirac [2] and by Frenkel [3] and their extension to include external perturbations has been presented by Karplus and Kolker [4] in the uncoupled approximation and by Thouless [5] and McLachlan and Ball [6] in the coupled approximation. The uncoupled approximation has been used by Karplus and Kolker [4] to calculate refractive indices and long range forces but the equations presented for the coupled approximation do not lend themselves to ready solution. As in time-independent theory the coupled approximation is the more accurate Dalgarno [7] and an alternative formulation of the coupled approximation is needed.

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*Numbers in [] throughout the text represent reference numbers.

THE TIME-DEPENDENT HARTREE-FOCK APPROXIMATION

The wave function $\Psi^{(0)}(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N)$ of a closed shell N electron system with electron position vectors \underline{r}_i is written in the Hartree-Fock approximation as

$$\Psi^{(0)}(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N) = A \prod_{i=1}^N U_i^{(0)}(\underline{r}_i) \quad (1)$$

where A is the normalized antisymmetrising operator and $U_i^{(0)}(\underline{r}_i)$ is the Hartree-Fock orbital. $\Psi^{(0)}$ satisfies the time-independent equation

$$F \Psi^{(0)} = E_F^{(0)} \Psi^{(0)} \quad (2)$$

in which the Fock Hamiltonian operator is given by

$$F = \sum_{i=1}^N H_i - \sum_{i < k} \sum \int \{ \beta_{ik} - \alpha_{ik} \} | U_i^{(0)}(\underline{r}_i) |^2 d\underline{r}_i \quad (3)$$

$$E_F^{(0)} = \sum_{i=1}^N \epsilon_i^{(0)} - \sum_{i < k} \sum \int \{ \beta_{ik} - \alpha_{ik} \} | U_i^{(0)}(\underline{r}_i) |^2 d\underline{r}_i \quad (4)$$

where

$$H_i = -\frac{1}{2} \nabla_i^2 - \frac{Z}{r_i} + \sum_{k=1}^N \{ \beta_{ik} - \alpha_{ik} \} \quad (5)$$

Z being the nuclear charge,

$$\beta_{ik} = \int \frac{| U_k(\underline{r}_k) |^2 d\underline{r}_k}{|\underline{r}_i - \underline{r}_k|} \quad (6)$$

and

$$\alpha_{ik} U_t(\underline{r}_i) = \int \frac{U_k^*(\underline{r}_k) U_t(\underline{r}_k) d\underline{r}_k}{|\underline{r}_i - \underline{r}_k|} U_k(\underline{r}_i) \quad (7)$$

α_{ik} vanishes unless the spins associated with U_k and U_i are parallel and it operates only on functions of \underline{r}_i . The spin orbitals $U_i(\underline{r}_i)$ satisfy the equations

$$H_i U_i^{(o)}(\underline{r}_i) = \epsilon_i^{(o)} U_i^{(o)}(\underline{r}_i) \quad (8)$$

Equation (2) can be written alternatively in the time-dependent form

$$\left\{ F - i\hbar \frac{\partial}{\partial t} \right\} \Phi^o(\underline{r}_1, \underline{r}_2, \dots, \underline{r}_N, t) = 0 \quad (9)$$

with solution

$$\Phi^{(o)}(\underline{r}, t) = \Psi^{(o)}(\underline{r}) \exp(-i E_F^{(o)} t / \hbar) \quad (10)$$

We now apply an external time-dependent perturbation

$$V(\underline{r}, t) = \lambda \left\{ \exp(i\omega t) + \exp(-i\omega t) \right\} \sum_{i=1}^N v_i(\underline{r}_i) \quad (11)$$

and proceed to solve the perturbed time-dependent equation

$$\left\{ F + V - i\hbar \frac{\partial}{\partial t} \right\} \Phi(\underline{r}, t) = 0 \quad (12)$$

within the Hartree-Fock approximation scheme. We expand according to

$$\Phi(\underline{r}, t) = \exp(-i E_F^{(0)} t/\hbar) A \prod_{i=1}^N \left\{ U_i^{(0)}(\underline{r}_i) + \lambda U_{i+}^{(1)}(\underline{r}_i) \exp(i\omega t) + \lambda U_{i-}^{(1)}(\underline{r}_i) \exp(-i\omega t) + \dots \right\} \quad (13)$$

and in order that (13) be normalized to first order in λ we require that

$$\langle U_i^{(0)}(\underline{r}_i) | U_{i+}^{(1)}(\underline{r}_i) \rangle + \langle U_{i-}^{(1)}(\underline{r}_i) | U_i^{(0)}(\underline{r}_i) \rangle = 0 \quad (14)$$

and

$$\langle U_i^{(0)}(\underline{r}_i) | U_{i-}^{(1)}(\underline{r}_i) \rangle + \langle U_{i+}^{(1)}(\underline{r}_i) | U_i^{(0)}(\underline{r}_i) \rangle = 0 \quad (15)$$

To solve (12), we construct the functional

$$\begin{aligned} & \langle \Phi | F + V - \hbar \frac{\partial}{\partial t} | \Phi \rangle + \sum_{i=1}^N \sum_{j=1}^N \Delta_{ij} \langle U_i^{(0)}(\underline{r}_i) | U_j^{(0)}(\underline{r}_i) \rangle \\ & + \sum_{i=1}^N \eta_i \left\{ \langle U_i^{(0)}(\underline{r}_i) | U_{i+}^{(1)}(\underline{r}_i) \rangle + \langle U_{i-}^{(1)}(\underline{r}_i) | U_i^{(0)}(\underline{r}_i) \rangle \right\} \\ & + \sum_{i=1}^N \zeta_i \left\{ \langle U_i^{(0)}(\underline{r}_i) | U_{i-}^{(1)}(\underline{r}_i) \rangle + \langle U_{i+}^{(1)}(\underline{r}_i) | U_i^{(0)}(\underline{r}_i) \rangle \right\} \end{aligned} \quad (16)$$

where Δ_{ij} , η_i and ζ_i are Lagrange multipliers. For closed shell systems we may effect a unitary transformation such that

$$\Delta_{ij} = \delta_{ij} \quad \chi_{ij} \equiv \delta_{ij} \chi_i \quad (17)$$

and we may write

$$\eta_i = \lambda \left\{ \eta_{i+}^{(1)} \exp(i\omega t) + \eta_{i-}^{(1)} \exp(-i\omega t) \right\} + \dots \quad (18)$$

$$\zeta_i = \lambda \left\{ \zeta_{i+}^{(1)} \exp(i\omega t) + \zeta_{i-}^{(1)} \exp(-i\omega t) \right\} + \dots \quad (19)$$

$$\chi_i = \left\{ \chi_{i+}^{(1)} \exp(i\omega t) + \chi_{i-}^{(1)} \exp(-i\omega t) \right\} + \dots \quad (20)$$

Varying the function (16) independently with respect to the orbitals $U_i^{(0)}$, $U_{i+}^{(1)}$ and $U_{i-}^{(1)}$ to find a stationary value, expanding in powers of λ and equating the coefficients of $\exp(i\omega t)$ and $\exp(-i\omega t)$ to zero yields the unperturbed equation

$$(H_i - \epsilon_i^{(0)}) U_i^{(0)}(\mathbf{r}_i) = 0 \quad (21)$$

and the coupled first order perturbed equations

$$\begin{aligned} & (H_i - \epsilon_i^{(0)} + \hbar\omega) U_{i+}^{(1)}(\mathbf{r}_i) \\ & + \left\{ v_i(\mathbf{r}_i) + v_{i+}^{(1)}(\mathbf{r}_i) + \sum_{j \neq i} \langle U_j^{(0)}(\mathbf{r}_i) | v_{j+}^{(1)}(\mathbf{r}_i) | U_j^{(0)}(\mathbf{r}_i) \rangle \right. \\ & \left. + \hbar\omega \sum_{j \neq i} \langle U_j^{(0)}(\mathbf{r}_i) | U_{j+}^{(1)}(\mathbf{r}_i) \rangle + \chi_{i+}^{(1)} \right\} U_i^{(0)}(\mathbf{r}_i) = 0 \end{aligned} \quad (22)$$

$$\begin{aligned} & (H_i - \epsilon_i^{(0)} - \hbar\omega) U_{i-}^{(1)}(\mathbf{r}_i) \\ & + \left\{ v_i(\mathbf{r}_i) + v_{i-}^{(1)}(\mathbf{r}_i) + \sum_{j \neq i} \langle U_j^{(0)}(\mathbf{r}_i) | v_{j-}^{(1)}(\mathbf{r}_i) | U_j^{(0)}(\mathbf{r}_i) \rangle \right. \\ & \left. - \hbar\omega \sum_{j \neq i} \langle U_j^{(0)}(\mathbf{r}_i) | U_{j-}^{(1)}(\mathbf{r}_i) \rangle + \chi_{i-}^{(1)} \right\} U_i^{(0)}(\mathbf{r}_i) = 0 \end{aligned} \quad (23)$$

where

$$V_{i\pm}^{(1)}(\underline{r}_i) = \sum_{k=1}^N \left\{ \beta_{ik\pm}^{(1)} - \alpha_{ik\pm}^{(1)} \right\} \quad (24)$$

with

$$\beta_{ik\pm}^{(1)} = \int d\underline{r}_k \frac{\left\{ U_k^{(0)*}(\underline{r}_k) U_{k\pm}^{(1)}(\underline{r}_k) + U_{k\mp}^{(1)*}(\underline{r}_k) U_k^{(0)}(\underline{r}_k) \right\}}{|\underline{r}_i - \underline{r}_k|} \quad (25)$$

and

$$\alpha_{ik\pm}^{(1)} = \int d\underline{r}_k \frac{\left\{ U_t^{(1)}(\underline{r}_i) \left[U_{k\mp}^{(1)*}(\underline{r}_k) U_t(\underline{r}_k) U_k^{(0)}(\underline{r}_i) + U_k^{(0)*}(\underline{r}_k) U_t(\underline{r}_k) U_{k\pm}^{(1)}(\underline{r}_i) \right] \right\}}{|\underline{r}_i - \underline{r}_k|} \quad (26)$$

and $V_{i\pm}^{(1)}(\underline{r}_i)$ is given by a similar expression with the signs interchanged on the subscripts. The potentials $V_{i\pm}^{(1)}$ and $V_{i\mp}^{(1)}$ reflect the influence of the perturbing field and they couple together the solutions $U_{i\pm}^{(1)}$ and $U_{i\mp}^{(1)}$. The multipliers $\chi_{i\pm}^{(1)}$ and $\chi_{i\mp}^{(1)}$ are given immediately by (22) and (23) as

$$\chi_{i\pm}^{(1)} = - \sum_{j=1}^N \left\{ \left\langle U_j^{(0)}(\underline{r}_j) \left| V_{j\pm}^{(1)} \right| U_j^{(0)}(\underline{r}_j) \right\rangle \pm \hbar\omega \left\langle U_j^{(0)}(\underline{r}_j) \left| U_{j\pm}^{(1)}(\underline{r}_j) \right\rangle \right\} \quad (27)$$

and (22) and (23) simplify to

$$\begin{aligned} & (H_i - \epsilon_i^{(0)} \pm \hbar\omega) U_{i\pm}^{(1)}(\underline{r}_i) \\ & + \left\{ V_{i\pm}^{(1)}(\underline{r}_i) + v_i(\underline{r}_i) - \left\langle U_i^{(0)} \left| V_{i\pm}^{(1)} \right| U_i^{(0)} \right\rangle \pm \hbar\omega \left\langle U_i^{(0)} \left| U_{i\pm}^{(1)} \right\rangle \right\} U_i^{(0)}(\underline{r}_i) = 0 \end{aligned} \quad (28)$$

$V_{i\pm}^{(1)}$ In the uncoupled Hartree-Fock approximation, the potential terms are assumed to vanish.

THE REFRACTIVE INDEX OF HELIUM

The perturbing potential appropriate to the calculation of the refractive index or dynamic dipole polarizability of helium is

$$\sum_i v_i(\underline{r}_i) = r_1 \cos \theta_1 + r_2 \cos \theta_2 \quad (29)$$

and (28) reduces to

$$\left\{ -\frac{1}{2} \nabla^2 - \frac{2}{r} - \epsilon^{(0)} + \int \frac{|U^{(0)}(\underline{r}')|^2}{|\underline{r} - \underline{r}'|} d\underline{r}' \pm \hbar\omega \right\} U_{\pm}^{(1)}(\underline{r}) + \left\{ \int \frac{U^{(0)}(\underline{r}) U_{\pm}^{(1)}(\underline{r}') + U_{\mp}^{(1)}(\underline{r}') U^{(0)}(\underline{r}')}{|\underline{r} - \underline{r}'|} d\underline{r}' + r \cos \theta \right\} U^{(0)}(\underline{r}) = 0 \quad (30)$$

For the unperturbed orbital $U^0(\underline{r})$ we adopted the twelve term representation of Roothan, Sachs and Weiss [8] and wrote $U_{\pm}^{(1)}$ in the form

$$U_{\pm}^{(1)}(\underline{r}) = f_{\pm}(\underline{r}) \cos \theta U^{(0)}(\underline{r}) \quad (31)$$

We solved (30) by finding the stationary values of the functional

$$J_{\pm}^{\pm} = \pm \hbar\omega \langle U_{\pm}^{(1)} | U_{\pm}^{(1)} \rangle + \langle U_{\pm}^{(1)} | -\frac{1}{2} \nabla^2 - \frac{2}{r} - \epsilon^{(0)} + \int \frac{|U^{(0)}(\underline{r}')|^2}{|\underline{r} - \underline{r}'|} d\underline{r}' | U_{\pm}^{(1)} \rangle$$

$$\begin{aligned}
& + 2 \langle U_{\pm}^{(1)} | r \cos \theta | U^{(0)} \rangle \\
& + \langle U_{\pm}^{(1)} | \int \frac{U^0(r') U_{\pm}^{(1)}(r')}{|r - r'|} dr' | U^0 \rangle \\
& + 2 \langle U_{\pm}^{(1)} | \int \frac{U^0(r') U_{\pm}^{(1)}(r')}{|r - r'|} dr' | U^0 \rangle \quad (32)
\end{aligned}$$

for trial functions

$$f_{\pm}(r) = \sum_{i=1}^m a_{i\pm} r^i \quad (33)$$

a procedure which leads to the set of equations

$$\begin{array}{|c|c|} \hline X^+ & L \\ \hline L & X^- \\ \hline \end{array} \begin{array}{|c|} \hline a^+ \\ \hline a^- \\ \hline \end{array} = - \begin{array}{|c|} \hline c \\ \hline c \\ \hline \end{array} \quad (34)$$

where a^+ , a^- and c are column vectors with elements a_{i+} , a_{i-} and $\frac{2}{3} \langle U^0 | r^{i+1} | U^0 \rangle$ and X^+ , X^- and L are m by m matrices with elements

$$X_{ij}^{\pm} = X_{ji}^{\pm} = \pm \frac{2\hbar\omega}{3} \langle U^0 | r^{i+j} | U^0 \rangle + \frac{1}{3} (2+i+j) \langle U^0 | r^{i+j-2} | U^0 \rangle + L_{ij} \quad (35)$$

and

$$\begin{aligned}
L_{ij} = L_{ij} = \frac{2}{9} \int dr |U^0(r)|^2 \left\{ r^i \int_0^r r'^{j+3} |U^{(0)}(r')|^2 dr' \right. \\
\left. + r^{i+3} \int_r^{\infty} r'^j |U^0(r')|^2 dr' \right\} \quad (36)
\end{aligned}$$

Expressing distance in units of the Bohr radius a_0 , the dynamic dipole polarizability of helium may be written

$$\alpha = 2 (J^+ + J^-) a_0^3 \quad (37)$$

A comparison of the values of the dynamic polarizability derived using the uncoupled and the coupled approximations is given in table 1. The uncoupled results are in close agreement with those obtained by Karplus and Kolker [4], based upon a less elaborate representation of the unperturbed orbital $U^0(r)$. Table 1 also includes the accurate values obtained by Chan and Dalgarno [9] based upon a twenty parameter correlated representation of the unperturbed wave function $\Psi^{(0)}$. Table 1 shows the coupled approximation is about 4% too small at the larger wavelengths, increasing to about 8% for the shorter wavelengths. The uncoupled approximation is everywhere about 8% too large. If the values are corrected by scaling factors chosen to ensure an accurate value for the static polarizability, the error in the scaled values is nowhere greater than 4% for the coupled results.

These results, taken together with calculations of static polarizabilities of heavier systems [10], [11] suggest that the coupled approximation may be successful in predicting frequency-dependent polarizabilities also.

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TABLE 1

FREQUENCY-DEPENDENT POLARIZABILITY OF HELIUM (10^{-24} cm^3)

Frequency (a.u.)	Wavelength \AA	Uncoupled	Accurate	Coupled
0.00		0.220	0.204	0.196
0.05	9112	0.221	0.205	0.196
0.10	4556	0.223	0.207	0.198
0.15	3037	0.226	0.210	0.201
0.20	2278	0.231	0.214	0.205
0.25	1822	0.237	0.220	0.210
0.30	1519	0.246	0.227	0.217
0.35	1302	0.257	0.237	0.226
0.40	1139	0.271	0.250	0.237
0.45	1012	0.289	0.267	0.252
0.50	911	0.314	0.289	0.272
0.55	828	0.348	0.320	0.299
0.60	759	0.398	0.366	0.337

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