Application of the finite element method to time-dependent quantum mechanics:
I. H and He in a laser field

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A finite element approach is described to solve the time-dependent Hartree–Fock equation of atoms in the presence of time-dependent electromagnetic fields. Time-dependent energy changes, ionization rates and high order nonlinear optical polarizabilities, χ_{2n+1} $(n \geqslant 0)$ for the atoms H and He have been calculated. The finite element method is shown to be easily adaptable to treat intense short pulses and includes automatically both bound and continuum electronic states.

1. Introduction

Time-dependent quantum mechanics involves solving the time-dependent Schrödinger equation (TDSE) which is a parabolic partial differential equation (PPDE). TDSEs occur naturally whenever one deals with time-dependent perturbation such as laser fields. Thus present laser technology allows one to subject atoms and molecules to increasing radiation intensities so that eventually perturbation theory breaks down [1,2]. Since the atomic unit of the electronic field e/a_0^2 corresponds to a field intensity of 3.5×10^{16} W/cm^2 (W = watts) current fields approaching 10^{14} W/cm^2 will introduce nonperturbative effects such as above threshold ionization [3], laser-induced avoided crossings of molecular electronic potential curves [4,5].

One of the fundamental difficulties in describing nonperturbative time-dependent phenomena is the proper inclusion simultaneously of bound and continuum electronic states. In the case of the H atom, successful numerical calculations have been carried out by solving the TDSE using implicit finite difference (FD) methods

in view of the local nature of the potential in the problem [6,7]. Extension of these numerical methods to multielectron problems has proved to be difficult due to the nonlocal nature of the exchange interaction.

Another approach which can handle nonlocal potentials is a basis set expansion, with sufficient flexibility to enable one to span localized bound state functions to highly delocalized free electron functions. Such flexible basis sets can be found in finite element (FE) methods which are local in nature. It is well known that simple FD and FE methods result often in identical approximations [8,9]. Recent applications of FE methods to time independent quantum chemistry has shown that these methods are well suited to treating nonlocal potentials such as the exchange potential in Hartree–Fock (HF) methods for atoms [10,11] and recently molecules [12–14]. In particular, taking advantage of expansion in terms of Legendre polynomials onto elements, one can obtain high accuracy due to the optimal properties of these polynomials: Legendre polynomials are the best approximation of any function with respect to its norm in a finite domain [15].

Preliminary calculations of the time-dependent solution of the H atom excited by an intense short laser pulse using FE methods [16] have been shown to compare extremely well with previous FD methods. The latter calculations are basis set free, whereas the FE method involves local basis sets. Current development in time-independent basis-free quantum chemistry have shown these to be very promising [17,18]. Such methods have not yet been developed for time-dependent problems. In the present paper we describe the local basis FE method as applied to the solution of the time-dependent Hartree–Fock equation (TDHF) of atoms in the presence of time-dependent perturbations. Our test case will be the H and He atoms. We are currently extending the method to multielectron atoms and molecules.

2. Theory

The time-dependent Schrödinger equation (TDSE) is of the general form

$$i\frac{\partial}{\partial t}\Phi(r, t) = H(r, t)\Phi(r, t),\tag{1}$$

where H is the total time-dependent Hamiltonian ($(\hbar = 1)$). Putting a completely antisymmetrized product wave function $\Phi(r, t)$ into eq. (1), the usual TDHF equation is obtained [6]:

$$i\frac{\partial}{\partial t}\Psi_i(r_i, t) = (h_i + V^{el})\Psi_i(r_i, t),\tag{2}$$

where the $\Psi_i(r_i, t)$ are the time dependent orbitals. In linearly polarized laser fields and using polar coordinates, the external electromagnetic perturbation V^{el} is written as

$$V^{\text{el}} = E_0(t)r\cos(\theta)\sin(\omega t) = A(r,t)\cos(\theta),\tag{3}$$

$E_0(t)$ is called the pulse envelope for an electromagnetic field of frequency ω in the dipole approximation.

The single-electron Hamiltonian h_i is defined as

$$h_i = h_{i0} + J_i,\tag{4}$$

with a core Hamiltonian h_{i0},

$$h_{i0} = -\frac{1}{2}\left(\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r}\right) + \frac{L^2}{2r^2} - \frac{Z}{r},\tag{5}$$

and time-dependent Coulomb integrals $J_i(1,t)$,

$$J_i(1,t)\Psi_i(1,t) = \sum_j^n \int \frac{\Psi_j^*(2,t)\Psi_j(2,t)}{r_{ij}}\,dV_2\Psi_i(1,t).\tag{6}$$

Since we limit ourselves to He, we do not need exchange integrals in the case of $S_z = 0$, although as noted below, the final equations over basis sets appear similar to the exchange case. We note that the Coulomb integrals become time dependent as opposed to standard Hartree–Fock theory. In the case of the He atom, n in eq. (6) is equal to 1. The one-electron wave function in eq. (2) can be expanded in terms of radial and spherical harmonic functions:

$$\Psi_i(1,t) = \sum_l^{l_{\max}} R_l(r,t)Y_l(\theta,\phi),\tag{7}$$

where $l_{\max}$ is the maximum state number used to expand wave functions. For linearly polarized light, $m_l = 0$ in eq. (7) and is suppressed in the notation of the Y's. Substituting eq. (7) into eq. (2) we obtain the coupled equations

$$(h_{i0} + J_i + V^{\text{el}})\sum_l^{l_{\max}} R_l(r,t)Y_l(\theta,\phi) = i\frac{\partial}{\partial t}\sum_l^{l_{\max}} R_l(r,t)Y_l(\theta,\phi).\tag{8}$$

Defining

$$J_{ll'}(t) = \langle Y_{l'}(\theta,\phi)|J_i(1,t)|Y_l(\theta,\phi)\rangle,\tag{9}$$

and using the orthogonality relation $\langle Y_l|Y_{l'}\rangle = \delta_{ll'}$, eq. (8) is transformed after simple manipulation into

$$h_{i0}(l)R_l(r,t) + \sum_{l'}^{l_{\max}}(J_{ll'} + G_{ll'})R_{l'}(r,t) = i\frac{\partial}{\partial t}R_l(r,t),\tag{10}$$

where $G_{ll'} = A(r,t) \times G_{l,l'}^a$ and

$$G_{l,l'}^a = \langle Y_l | \cos(\theta) | Y_{l'} \rangle$$

$$= \begin{cases} \dfrac{l}{[(2l+1)(2l'+1)]^{1/2}} & \text{if } l'+1 = l, \\[4mm] \dfrac{l+1}{[(2l+1)(2l'+1)]^{1/2}} & \text{if } l'-1 = l. \end{cases} \tag{11}$$

By choosing a finite element basis set for the radial functions,

$$R(r, t) = \mathbf{X}(r)\mathbf{C}(t), \tag{12}$$

where $\mathbf{X}(r)$ is the vector for the FE basis set, and $\mathbf{C}(t)$ is the matrix for the time-dependent coefficients. Derivativing the eq. (12) with respect to time, one obtains

$$\frac{\partial R(r, t)}{\partial t} = \mathbf{X}(r)\frac{\partial \mathbf{C}(t)}{\partial t}, \tag{13}$$

Substituting eqs. (12) and (13) into eq. (10), we have

$$h_{i0}(l)\mathbf{X}(r)\mathbf{C}_l(t) + \sum_{l'}^{l_{max}}(J_{ll'} + G_{ll'})\mathbf{X}(r)\mathbf{C}_{l'}(t) = \mathrm{i}\mathbf{X}(r)\frac{\partial}{\partial t}\mathbf{C}_l(t). \tag{14}$$

Left multiple $\mathbf{X}^+$ in eq. (14) and defining

$$B_0(l) = \mathbf{S}^{-1}\mathbf{X}^+ h_{i0}(l)\mathbf{X}, \tag{15}$$

where $\mathbf{S}^{-1}$ is the inverse of the FE overlap matrix $\mathbf{X}^+\mathbf{X}$ between the FE basis sets, $h_{i0}(l)$ is defined in eq. (5), and $\mathbf{X}^+ h_{i0}(l)\mathbf{X}$ is a Hamiltonian matrix with respect to the FE basis set. For the H atom, $\mathbf{X}^+ h_{i0}(l)\mathbf{X}$ is a time-dependent matrix involving time-independent kinetic energy and Coulomb integrals over the FEs but a time-dependent radiation interaction matrix, eq. (3). For the He atom, the Coulomb repulsion becomes time dependent. Substituting eq. (15) into eq. (14), we obtain the following equation:

$$B_0(l)\mathbf{C}_l(t) + \sum_{l'}^{l_{max}}(J_{s,ll'}(t) + G_{s,ll'}(t))\mathbf{C}_{l'}(t) = \mathrm{i}\frac{\partial}{\partial t}\mathbf{C}_l(t), \tag{16}$$

where $J_{s,ll'} = \mathbf{S}^{-1}\mathbf{X}^+ J_{ll'}\mathbf{X}$ and $G_{s,ll'} = \mathbf{S}^{-1}\mathbf{X}^+ G_{ll'}\mathbf{X}$. Equation (16) can be rewritten in matrix form as

$$\begin{pmatrix} B_0(0) + J_{s,00} & j_{s,01} + G_{s,01} & \cdots & J_{s,0n} \\ J_{s,10} + G_{s,10} & B_0(1) + J_{s,11} & \cdots & J_{s,1n} \\ \vdots & \vdots & \ddots & \vdots \\ J_{s,n0} & J_{s,n1} & \cdots & B_0(n) + J_{s,nn} \end{pmatrix} \begin{pmatrix} \mathbf{C}_0 \\ \mathbf{C}_1 \\ \vdots \\ \mathbf{C}_n \end{pmatrix} = \mathrm{i}\frac{\partial}{\partial t}\begin{pmatrix} \mathbf{C}_0 \\ \mathbf{C}_1 \\ \vdots \\ \mathbf{C}_n \end{pmatrix}. \tag{17}$$

Note that because of radiative selection rules $\Delta l = \pm 1$, the matrix elements of G_s occupy only the first off-diagonal positions, i.e., G_s is a tridiagonal matrix.

Using a time-dependent basis set, based on Legendre polynomials, the FE set which has the virtue of being flexible and highly accurate, one solves the ordinary differential equations (ODE) (17), iteratively with appropriate initial condition, i.e. $\Psi(r, 0)$ is the ground state. The time-dependent coefficient vector $\mathbf{C}(t)$ is propagated successively by a fourth order Taylor series expansion,

$$\mathbf{C}^{n+1} = \left(1 - \mathrm{i}\Delta t A - \frac{1}{2}\Delta t^2 A^2 + \mathrm{i}\frac{1}{3!}\Delta t^3 A^3 + \frac{1}{4!}\Delta t^4 A^4\right)\mathbf{C}^n, \tag{18}$$

where A is the Hamiltonian, the left matrix in eq. (17) (a Tchebycheff polynomials expansion gave similar results). We emphasize that the FE basis set, due to its flexibility can represent both bound and continuum states. The final wave function after a time t, $\Psi(r, t, E(t))$ is an implicit function of the electromagnetic field $E(t)$ and is next used to calculate the field-induced polarizability.

The calculation of the new time dependent Coulomb term $J_{nm}(t)$ is a key problem. We proceed as follows:

Substituting eq. (7) into eq. (6) we have in the case of He atom ($n = 1$)

$$J_i(1, t) = \sum_{K}^{l_{max}} \sum_{L}^{l_{max}} \int \frac{R_L^*(2, t) R_K(2, t)}{r_{12}} Y_K(2) Y_L(2)\, \mathrm{d}V_2. \tag{19}$$

We now expand the time-dependent radial function $R_L(2, t)$ in terms of the FE basis sets, X_r, with time-dependent coefficients $C_{Lr}(t)$,

$$R_L(2, t) = \sum_{r}^{n} C_{Lr}(t) X_r(2). \tag{20}$$

Substituting eq. (20) into eq. (19) the Coulomb term becomes in the FE bases

$$J_i(1, t) = \sum_{K}^{l_{max}} \sum_{L}^{l_{max}} \sum_{r}^{n} \sum_{s}^{n} C_{Lr}^*(t) C_{Ks}(t) \int \frac{X_r^*(2) X_s(2)}{r_{12}} Y_L(2) Y_K(2)\, \mathrm{d}V_2. \tag{21}$$

From eq. (21) one obtains new time-dependent matrix elements:

$$J_{ll'}^{pq}(t) = \langle X_p(1) Y_l(1)|J_i(1, t)|X_q(1) Y_{l'}(1)\rangle \tag{22a}$$

or

$$J_{ll'}^{pq}(t) = \sum_{L,K}^{l_{max}} \sum_{r,s}^{n} D_{Lr,Ks}(t)\langle pr|qs\rangle, \tag{22b}$$

with time-dependent density matrix elements

$$D_{Lr,Ks}(t) = \frac{N_L N_K}{2} C_{Lr}^*(t) C_{Ks}(t). \tag{23}$$

This is to be contrasted with time independent HF theory where the D's are time independent. N_L and N_K are the occupation numbers corresponding to symmetry L and K, respectively. The time-independent Coulomb integrals $\langle pr|qs\rangle$ are defined as

$$\langle pr|qs \rangle = \int \int X_p(1) X_q(1) X_r(2) X_s(2) \frac{1}{r_{12}} Y_K(2) Y_L(2) Y_l(1) Y_{l'}(1) \, dV_1 \, dV_2 . \quad (24)$$

These are the most general integrals which appear for He. Similar integrals would have appeared had we included proper exchange integrals. Clearly all time dependence is now contained in the density matrix elements, eq. (23). Expanding $1/r_{12}$ in terms of Legendre polynomials and for a linearly polarized laser field, eq. (3), then the integrals (24) become

$$\langle pr|qs \rangle = \sum_{\lambda=0}^{\infty} C_1^\lambda(l, l') C_2^\lambda(K, L) R^\lambda(pqrs) , \quad (25)$$

$$R^\lambda(pqrs) = \int \int X_p(1) X_q(1) X_r(2) X_s(2) r_1^2 r_2^2 \frac{r_<^\lambda}{r_>^{\lambda+1}} \, dr_1 \, dr_2 , \quad (26)$$

$$C_i^\lambda(i = 1, 2) = \int_{-1}^{1} Y_l(u) Y_m(u) Y_n(u) \, du , \quad (27)$$

$$C_i^\lambda(m, n) = [(2l + 1)(2m + 1)]^{1/2} (-1)(s - m)$$
$$\times \frac{n!(2s - 2n)! s!}{(s - l)!(s - m)!(s - n)!(2s + 1)!}$$
$$\times \sum_w (-1)^w \frac{(l + w)!(m + n - w)!}{w!(l - w)!(m - n + w)!(n - w)!} .$$

The conditions on $C_i^\lambda(m, n)$ are [19]

$$C_i^\lambda(m, n) = \begin{cases} C_i^\lambda(m, n) & \text{if } (l + m + n) = \text{even number and } (m + n) \geqslant (m - n); \\ 0 & \text{otherwise}, \end{cases}$$
$$(29)$$

and $2s = (l + m + n)$.

In summary, the TDHF equations (2) which are coupled nonlinear PPDEs have been reduced by use of the FE basis expansion (7), (12) to ordinary differential equations, ODEs.

3. Results and discussion

In our previous work [16], we showed that the FE basis successfully gave highly accurate energies for the simple H atom. In all our calculations on the He, the atom is placed in the center of the sphere with a radius of 100 au. The radius is divided into 18 finite elements. The number of basis functions used is 50 and the maximum number of states l_{max} was set at 6. Using these values we obtain a total energy of

−77.83 eV with the corresponding orbital energy of −24.96 eV in the initial (ground) state of He atom. This compares very well with the Hartree–Fock limit of −77.87 eV and the true ionization potential of −24.58 eV of the He atom [14]. Extending the l_{max} to higher values gave the HF limit at about $l_{max} = 10$.

3.1. ENERGIES AND IONIZATION RATES

All energies are changed as the wave function is propagated in time according to the scheme (18). In the initial state, the two electrons occupy the same 1s orbitals with opposite spin. These electrons are then excited to various high energy levels with time. Therefore the Coulomb interaction between electrons, as measured by the Coulomb integrals (19), depends on time in the case of He atom and gets weaker as the atom ionizes. As the interelectronic repulsion becomes weaker, the orbital energy decreases also, from −24.9 to −26.7 eV, as shown in fig. 1. The decrease of the orbital energy with time corresponds to an increase of the ionization potential of He, making it more difficult for the atom to ionize. Oscillations in the orbital energy occur with time due to return of electron density to the ground state which are called Rabi oscillations [16].

The variation of the total energy with time is given in fig. 2. It is clear that the total energy increases with time. The two electrons occupy 1s orbitals in the initial state where the system is most stable. The electrons then are excited continuously
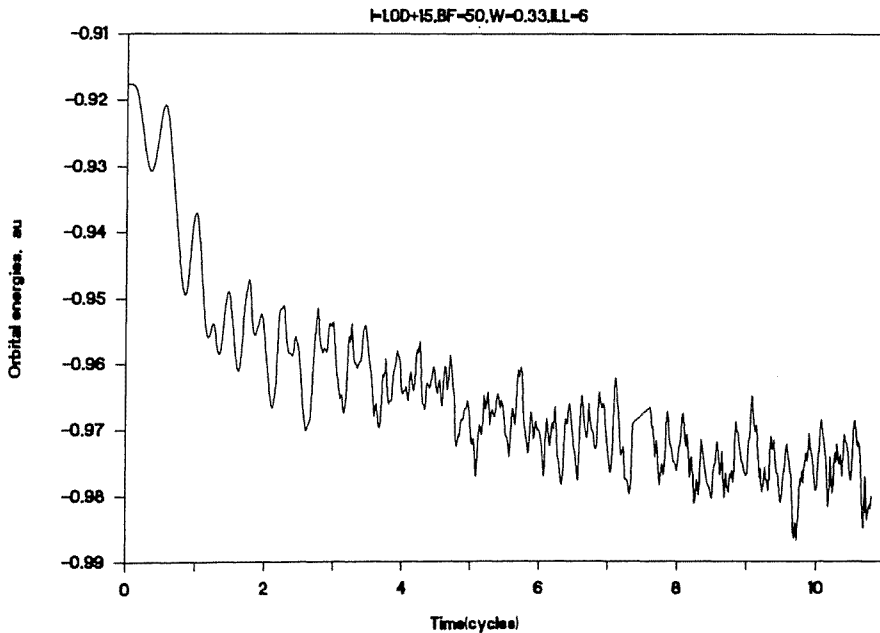

Fig. 1. Orbital energy as a function of time, for the intensity $I = 10^{15}$ W/cm^2 and frequency $\omega = 0.33$ au. (1 optical cycle $= 4.6 \times 10^{-16}$ s.)
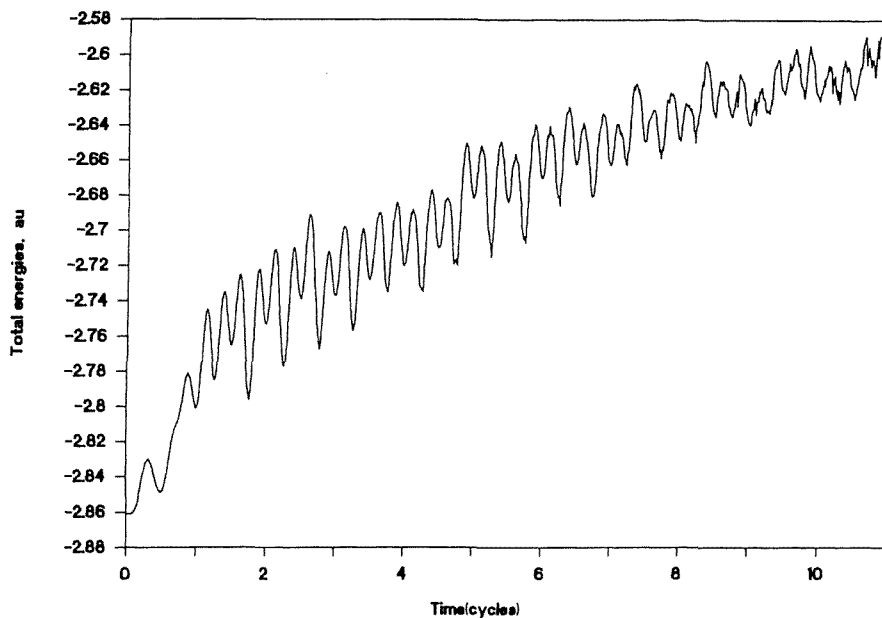
Fig. 2. Total energy as a function of time with the same condition as in fig. 1.

under the interaction with the external field. The atom becomes less stable with time and the energy increases consequently as higher bound and continuum orbitals become admixed to the initial 1s state.

The ionization rates Γ obtained for various intensities and frequencies are shown in table 1 together with other known results based on FD methods. These were calculated for long time using the formula $-\ln P_{1s}(t) = \Gamma t$, where $P_{1s}(t)$ is the 1s probability. Both FD and FE results agree very well.

3.2. POLARIZABILITIES

Most previous calculations of polarizabilities of atoms and small molecules, generally rely on time independent iterations or perturbations, for example H [20–

Table 1
Ionization rates Γ of He atom for various values of intensity I and frequency ω.

I (W/cm^2)	ω (au)	Γ (s^{-1}) this paper	Γ (s^{-1}) previous work
4×10^{15}	0.0428		0.47×10^{12} [a]
–	0.0856	0.9×10^{12}	0.90×10^{12} [a]
–	0.10	1.1×10^{12}	
10^{15}	0.0856	1.7×10^{13}	1.9×10^{13} [a]
–	0.10	1.3×10^{13}	
–	0.33	2.1×10^{13}	2.6×10^{13} [a]

[a] Ref. [6].

23], He [24,25], noble gases [26–28], alkali metals [29] and small molecules [30,31]. Here we present the results of calculations based on numerical solutions of the TDSE, using FE basis sets.

In general, the polarizability or dipole moment induced in an atom or molecule by a uniform external field $E(t)$ can be expressed in a power series expansion [32],

$$P(t) = \chi_1 E(t) + \chi_3 E(t)^3 + \chi_5 E(t)^5 + \chi_7 E(t)^7 + \dots, \tag{30}$$

where $\chi_1 = \alpha$, $\chi_3 = \gamma/3!$, $\chi_5 = \delta/5!$ and $\chi_7 = \zeta/7!$, etc., are the general nonlinear susceptibilities. The above expression applies to an atom which is spherically symmetric. The coefficients α, γ, δ and ζ usually are termed hyperpolarizabilities.

(i) Validity of power expansion (30)

In the present case, we verify the validity of expression (30). We first test our new method for the hydrogen atom. Clearly, this perturbation expression remains valid when $P(t)$ and $E(t)$ are synchronized, i.e. in phase. We show this perfect synchronization for the H atom at the frequency $\omega = 0.0428$ au and intensity $I = 10^{13}$ W/cm^2 in fig. 3. The external field used is that defined in eq. (3) with the pulse shape $E_0(t)$ taken as

$$E(t) = \begin{cases} \text{linear increase} & (t \leqslant 1) \text{ optical cycle}; \\ E_0 & (t > 1) \text{ optical cycle}, \end{cases} \tag{31}$$
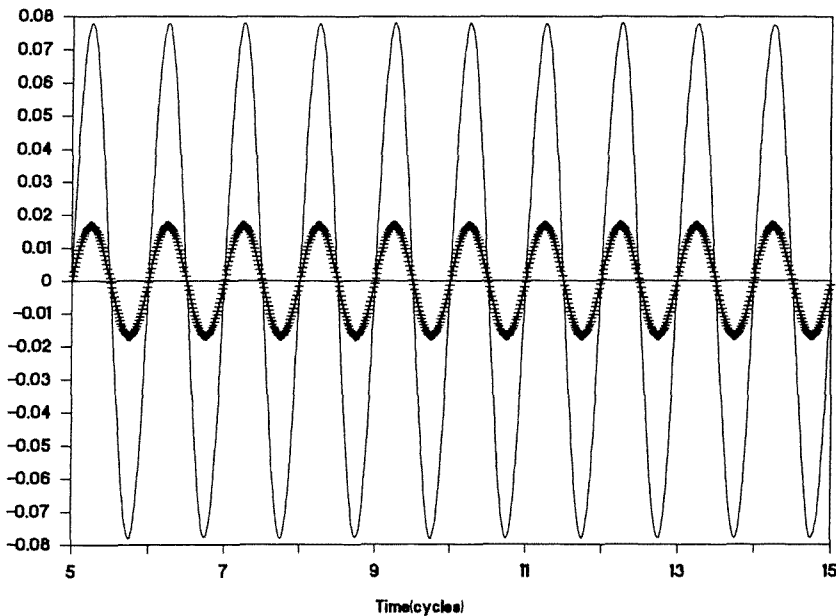

Fig. 3. Comparison of the dipole moment (solid line) with the laser field (crossed line) at the intensity $I = 10^{13}$ W/cm^2 and frequency $\omega = 0.0428$ au for the H atom. (1 optical cycle = 3.5×10^{-15} s.)

where 1 optical cycle $= (\pi/\omega) \times 4.8 \times 10^{-17}$ s. However, at the intensity $I = 1.75$ $\times 10^{14}$ W/cm^2 and frequency $\omega = 0.2$ au, one sees in fig. 4 complete dephasing of the polarizability $P(t)$ with respect to the incident field due to high excitation and ionization. Detailed calculations show that the rate of turn-on of the laser field does not affect this phenomenon. The dephasing of the field induced polarizability clearly comes from real and virtual excitations, such that higher frequency components, with frequency greater than the external field are introduced. Similar calculations of the dipole moment of the He atom with time shows that the dipole moment and external laser field are also exactly in phase for the intensity $I = 2.0 \times 10^{14}$ W/cm^2 and frequencies $\omega = 0.1$ au and 0.17 au.

(ii) H-atom hyperpolarizabilities

Equation (30) can be used to obtain the nonlinear optical susceptibilities χ_{2n+1} in the intensity regime where the field-induced dipole moment and the incident field are in phase. Alternatively, one can use the frequency-dependent polarizabilities, $P(\omega)$ [32], which for plane wave fields $(E_0(t) = E_0)$ gives after Fourier transforming eq. (30)

$$P(\omega) = \chi_1 E_0, \quad P(3\omega) = \chi_3 E_0^3, \tag{32}$$

$$P(5\omega) = \chi_5 E_0^5, \quad P(7\omega) = \chi_7 E_0^7. \tag{33}$$
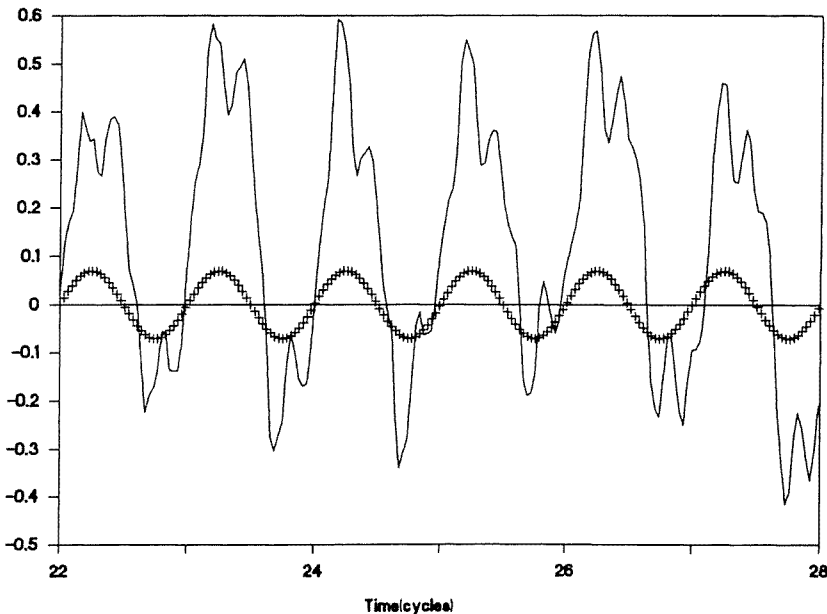

Fig. 4. Comparison of the dipole moment (solid line) with the laser field (crossed line) at the intensity $I = 1.75 \times 10^{14}$ W/cm^2 and frequency $\omega = 0.02$ au for the H atom. (1 optical cycle $= 7.5 \times 10^{-16}$ s.)

We therefore used two methods to calculate the susceptibilities or hyperpolarizabilities. In the first time-dependent method, a singular value decomposition by a general linear square algorithm [33] was used for various frequencies and intensities. This is reported in table 2 with appropriate comparison to known results [34–37]. These time-dependent results (eq. (30)) are complemented by the frequency-dependent method (32), (33).

We found in general that the time-dependent method was easier to apply, allowing one to go to lower intensities. Thus in the low intensity regime, a first fit at various intensities to the truncated expression $P(t) = \chi_1 E + \chi_3 E^3$ gave values of χ_1 and χ_3 which were found to extrapolate linearly to χ_{01} and χ_{03}, the zero field limit. The residual $R(t) = P(t) - \chi_{01} E - \chi_{-3} E^3 = \chi_5 E^5 + \chi_7 E^7$ was then fit by the same least squares method, so that values of χ_5 and χ_7 were obtained. It was found that the residual $R(t)$ was not in phase with the incident field, indicating sensitivity of these higher susceptibilities to Rabi oscillations from high lying excitations. The Fourier method, on the other hand, necessitates a lot of calculations at high intensities in order to get reasonable peak intensities at the harmonic frequencies $(2n + 1)\omega$, in addition to requiring many more field cycles in order to obtain well defined peaks. The results in table 2 were obtained from fitting 12 intensities between 0.5 and 5×10^{13} W/cm^2 for $P(t)$ and using 6 intensities between 1.5 and 5×10^{13} W/cm^2 for $P(\omega)$. The time-dependent and frequency-dependent results for α, γ, δ and ζ were found to agree quite well between themselves and also with previous perturbative calculations, especially in the case of the lower hyperpolarizabilities α and γ. For the higher parameters δ and ζ, the time-dependent method generally gave results closer to the perturbative results. The two nonlinear hyperpo-

Table 2

Hyperpolarizabilities of the hydrogen atom. Units: au; $(n) = 10^n$.

ω	α	γ	δ	ζ
Fitting method				
0.0428	4.32	1.64(3)	4(7)	1(12)
0.0656	4.40	2.20(3)	1(8)	4(12)
Fourier method				
0.0428	4.47	2.19(3)	4(7)	6(12)
0.0656	4.53	3.18(3)	2(8)	2(13)
Previous results				
0.0428	4.55 [a]	1.69(3) [a]	1(7) [a]	
0.0428		1.67(3) [b]	1(7) [b]	–
0.0656	4.62 [c]	2.38(3) [c]		
0.0656		2.48(3) [b]	1(8) [b]	
0.0	4.50 [c]	1.33(3) [c]		

[a] Ref. [37].
[b] Ref. [35].
[c] Ref. [34].

larizabilities, δ and ζ, which involve sixth order and eighth order photon virtual transition respectively in perturbative treatments [32], are expected to be sensitive to highly excited states including continuum states. Such states are difficult to include in perturbative calculations but are automatically included in the present FE basis method.

(iii) He-atom polarizabilities

The nonlinear or hyperpolarizabilities α, γ, δ and ζ for He were obtained (table 3) using the fitting method based on the time-dependent polarizability $P(t)$, eq. (30). It was found that in order to obtain significant frequency dependent polarizabilities $P(\omega)$, eq. (32), intensities higher than 10^{14} W/cm^2 were required. The time-dependent procedure allowed therefore to obtain results in the lower intensity regime between 10^{13} and 10^{14} W/cm^2. The present results were obtained from calculations of $P(t)$ at six intensities from 10^{13} to 2.0×10^{14} W/cm^2. Again the calculated results of the hyperpolarizabilities were found to agree quite well with previous perturbative results for α, γ and δ. We note that our value of ζ is a new result.

4. Conclusion

The present work shows that FE basis sets which are local in nature are ideally suited to treat time-dependent problems for time dependent perturbations which lead to high excitations into Rydberg and continuum states. Thus using a limited FE basis set expansion based on the optimal properties of Legendre polynomials [15], we have obtained ionization rates of H and He which agree with previous FD calculations. Furthermore, the laser field induced dipole moments calculated from the total time-dependent function enable one to extract high order nonlinear

Table 3
Hyperpolarizabilities of the helium atom. Units: au; $(n) = 10^n$.

ω	α	γ	δ	ζ
Fitting method				
0.10	1.43	60.0	4(5)	3(9)
0.17	1.46	130.0	2(6)	2(10)
Previous results				
0.086		90.6 [a]	4(5) [a]	
0.1312		141.6 [a]	2(6) [a]	
0.17		76.8 [b]	3(6) [b]	
0.0	1.38 [c]	2.44 [c]	10.6 [c]	

[a] Ref. [35].
[b] Ref. [36].
[c] Ref. [37].

polarizabilities, χ_{2n+1} $(n \geqslant 0)$. These high order polarizabilities involve multiple excitations which will in principle involve continuum states. Our numerical calculations of low order hyperpolarizabilities agree well with previous perturbative calculations and offer the possibility of calculating high order ones since our basis sets, which allow for calculation of ionization rates, therefore implicitly contain continuum state contributions. We are currently extending the FE method to the time-dependent quantum mechanics of polyelectronic atoms and molecules.

Acknowledgements

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