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**Towards a time-dependent description of electron - atom/ion
collisions: Two electron systems[†]**

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- autoionization of doubly excited states
- photoionization in the dipole approximation
- electron impact of atomic hydrogen; elastic, excitation, ionization

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Numerical Calculation of Correlated Wavefunctions for the Coulomb Three-body Problem

Consider two electrons moving in the field of an infinitely heavy nucleus of charge C . If the electrons have position vectors \vec{r}_1, \vec{r}_2 , the Hamiltonian

$$H = -\frac{1}{2}(\nabla_1^2 + \nabla_2^2) + \left(\frac{1}{r_{12}} - \frac{C}{r_1} - \frac{C}{r_2} \right), \quad (1)$$

where

$$r_{12} = (r_1^2 + r_2^2 - 2r_1r_2\cos\theta)^{\frac{1}{2}}, \quad (2)$$

and θ is the angle between \vec{r}_1 and \vec{r}_2 .

The exact nonrelativistic wavefunction for a state of total spin S and total orbital angular momentum L can be expanded as follows,

$$\Psi(\vec{r}_1, \vec{r}_2) = \Theta_{SM_S} \sum_{\ell=\varpi}^L \psi_{\ell}(\vec{r}_1, \vec{r}_2, \theta) \mathcal{Y}_{LM_L}(\ell, L + \varpi - \ell) \quad (3)$$

where Θ is a spin eigenfunction, and $\mathcal{Y}_{LM_L}(\ell, \ell')$ are the usual coupled spherical harmonics.

Then it is straightforward to derive a set of coupled equations satisfied by the functions ψ_ℓ , whose arguments are the three "dynamical" variables r_1 , r_2 and θ ,

$$[\mathbf{h}(\ell, L + \omega - \ell) - E]\psi_\ell = \sum_{\ell'} [v_{\ell\ell'}^{(1)} + v_{\ell\ell'}^{(2)}]\psi_{\ell'}. \quad (1)$$

The diagonal Hamiltonian has the obvious form

$$\mathbf{h}(\ell_1, \ell_2) = -\frac{1}{2} \left[\frac{\partial^2}{\partial r_1^2} + \frac{\partial^2}{\partial r_2^2} + \left(\frac{1}{r_1^2} + \frac{1}{r_2^2} \right) \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) \right] + \left[\frac{\ell_1(\ell_1 + 1)}{2r_1^2} + \frac{\ell_2(\ell_2 + 1)}{2r_2^2} \right], \quad (2)$$

while the coupling terms are given by

$$v_{\ell\ell'}^{(j)} = \frac{\mathcal{Z}_{\ell\ell'}^{(j)}(\theta)}{r_j^2} \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \quad (3)$$

for $j = 1, 2$. General formulae for the coefficients \mathcal{Z} have been obtained from angular momentum theory.

Each function is expanded in products of splines,

$$\psi_\ell(r_1, r_2, \theta) = \sum_{ijk} c_{ijk} u_i(r_1) u_j(r_2) w_k(\theta), \quad (4)$$

and the collocation principle is applied in the usual way to obtain the equations satisfied by the vector of $|\psi_\ell(r_{1\alpha}, r_{2\beta}, \theta_\gamma)\rangle$ on the collocation lattice.

The Basis-spline collocation method

We start with the time-dependent Schrödinger equation

$$H\psi = i\frac{\partial\psi}{\partial t}. \quad (1)$$

The wavefunction ψ is then expanded as

$$\psi(x, t) = \sum_k u_k(x)\psi^k(t) \quad (2)$$

where the u_k are a series of local functions known as basis splines and the ψ^k are the time-dependent expansion coefficients. The basis splines are piecewise continuous, differentiable polynomials of arbitrary order.

We now discretize the problem by demanding that the Schrödinger equation be obeyed exactly at a set of points $\{\xi_\alpha\}$ known as collocation points. Examining first the wavefunction, it is possible to make the definition

$$\psi_\alpha \equiv \psi(\xi_\alpha, t) = \sum_k u_k(\xi_\alpha)\psi^k(t). \quad (3)$$

We also make the definitions

$$B_{\alpha k} \equiv u_k(\xi_\alpha) \quad (4)$$

$$B^{\alpha k} \equiv [B_{\alpha k}]^{-1} \quad (5)$$

Next, examining the Schrödinger equation itself, if the Hamiltonian is given by

$$H = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x) \quad (1)$$

then putting the previous expansion into the Schrödinger equation gives

$$\sum_k \left(-\frac{1}{2} \frac{d^2 u_k}{dx^2} \psi^k + V u_k \psi^k \right) = i \sum_k u_k \dot{\psi}^k. \quad (2)$$

We now demand that this equation be obeyed exactly at the collocation points and include the transformation to the lowered indices, allowing us to write (2) as

$$\sum_{\beta} (T_{\alpha}^{\beta} + V_{\alpha}^{\beta}) \psi_{\beta} = i \dot{\psi}_{\alpha}, \quad (3)$$

where

$$T_{\alpha}^{\beta} = \sum_k -\frac{1}{2} B''_{\alpha k} B^{k\beta} \quad (4)$$

$$V_{\alpha}^{\beta} = V(\xi_{\alpha}) \delta_{\alpha}^{\beta} \quad (5)$$

and

$$B''_{\alpha k} = \left. \frac{d^2 u_k}{dx^2} \right|_{x=\xi_{\alpha}}. \quad (6)$$

He(2s²)

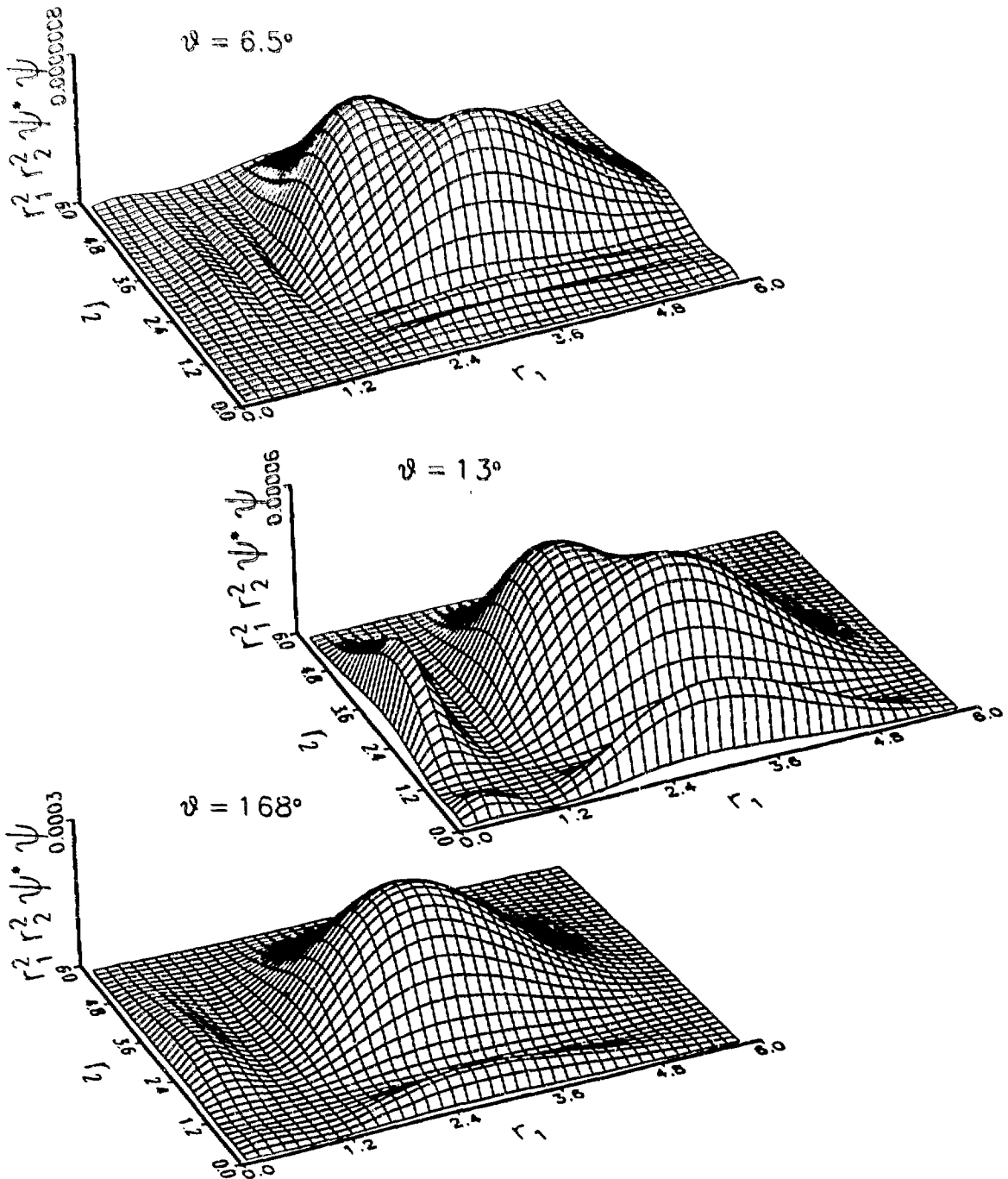


Fig. 1. The He(2s²) wavefunction at t = 0 a.u.

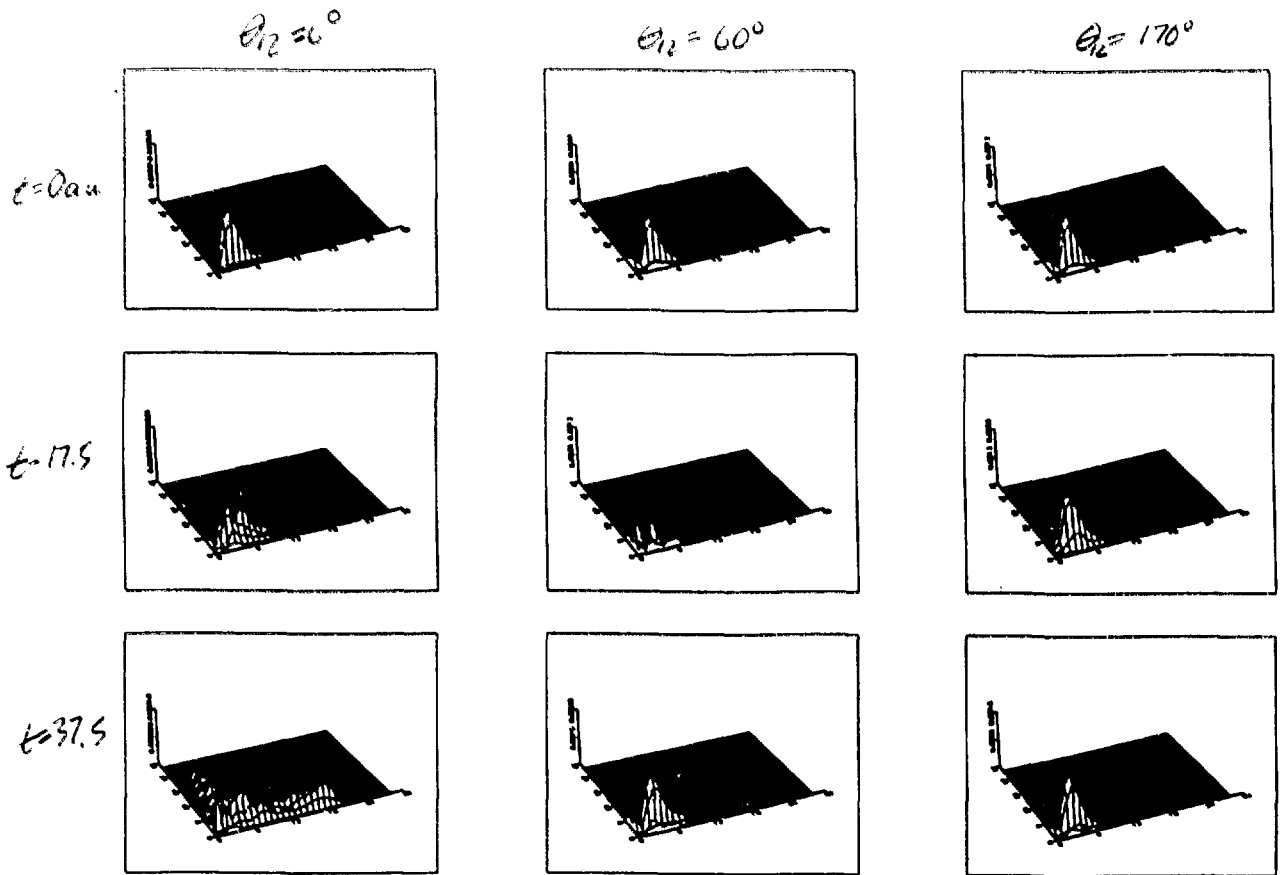


Fig. 2. The time evolution of the $He(2s^2)$ wavefunction is depicted for times $t = 0$, 17.5 and 37.5 a.u. at three values of θ_{12} , the angle between \vec{r}_1 and \vec{r}_2 . The action of the propagator is given by $\psi(t + \Delta t) = e^{-i\Delta t \mathcal{H}} \psi(t)$.

The correlation function is defined as

$$P(t) \equiv \langle \Psi(t) | \Psi(t=0) \rangle \quad (1)$$

(time dependent overlap of the time evolved wf with the initial wf). For an autoionizing state we expect that

$$P(t) = e^{-\Gamma t} \quad (2)$$

The spectral function is the Fourier transform of the correlation function,

$$P(E) = \int_{-\infty}^{+\infty} dt e^{iEt} P(t) \quad (3)$$

It will display resonances corresponding to the eigenvalues of the Hamiltonian. Line fitting techniques can refine the determination of the complex eigenvalue

$$E = \mathcal{E} + i\Gamma/2 \quad (4)$$

(see e.g. M Hermann and J Fleck, PRA **38**, 6000 (1980)).

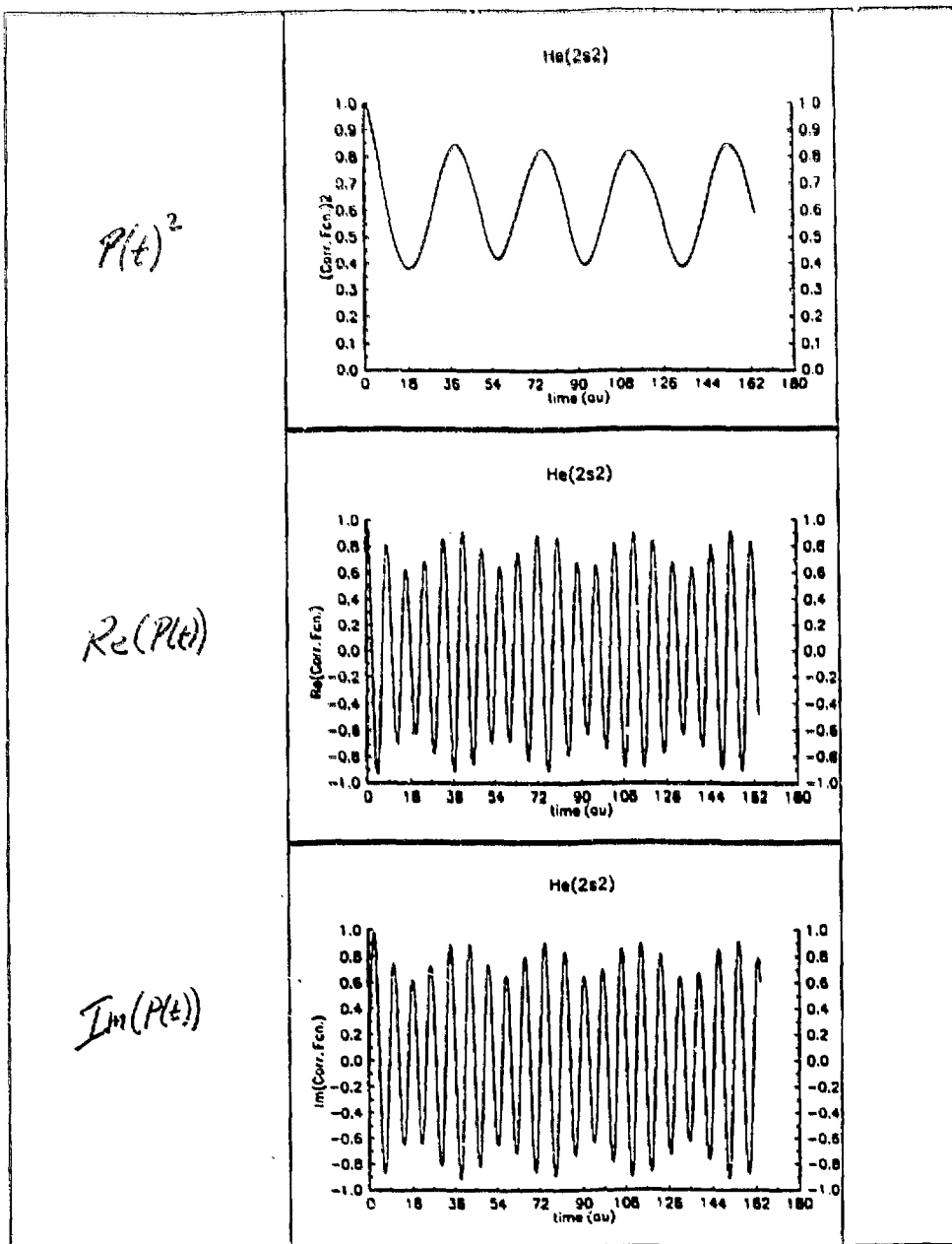


Fig. 3. The square of the correlation function and its real and imaginary parts for the time evolution of the $He(2s^2)$ state.

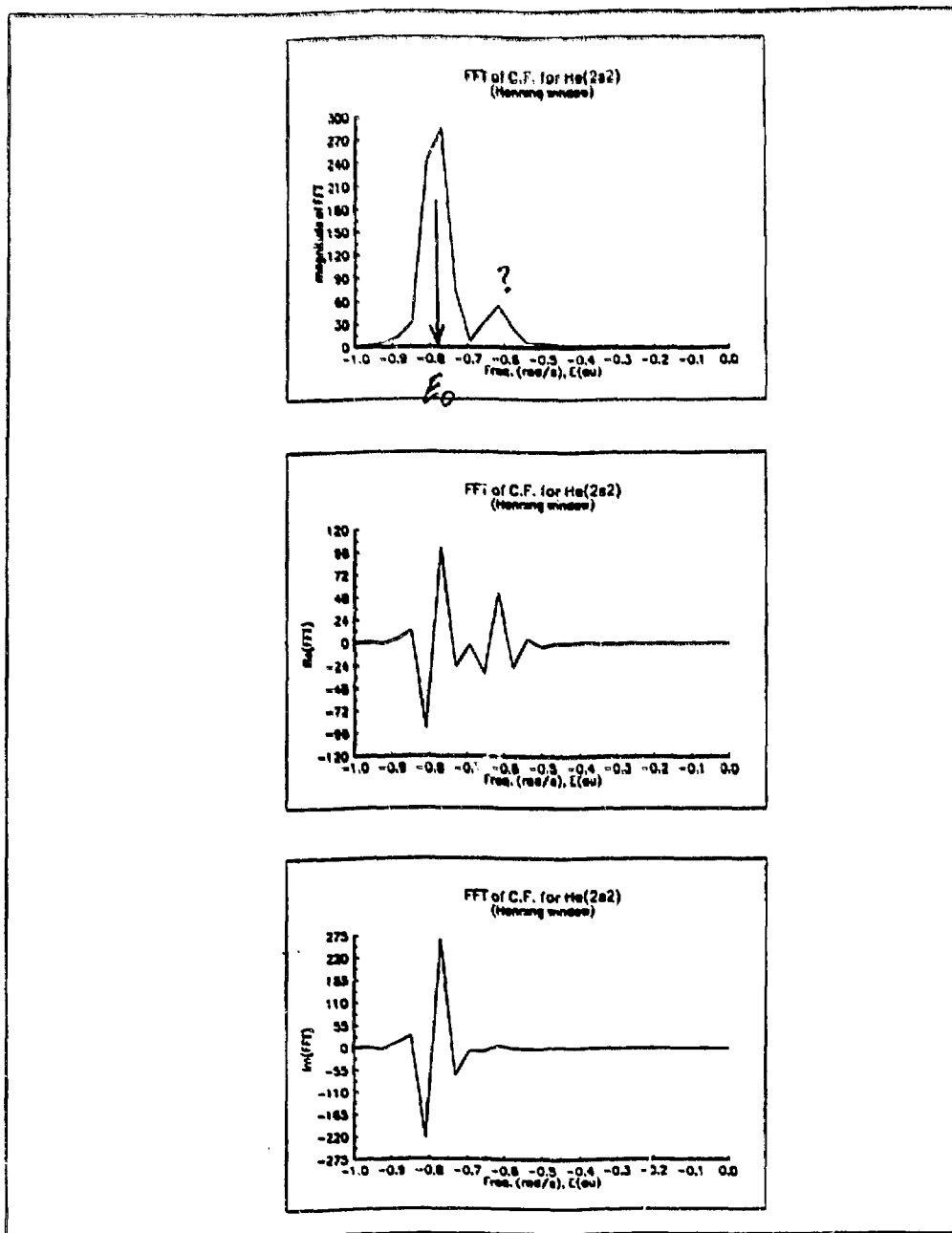


Fig. 4. The magnitude of the Fourier transform of the correlation function and its real and imaginary parts. Line-shape fitting to the large peak gives an accurate value for the energy eigenvalue and decay width for the $He(2s^2)$ state.

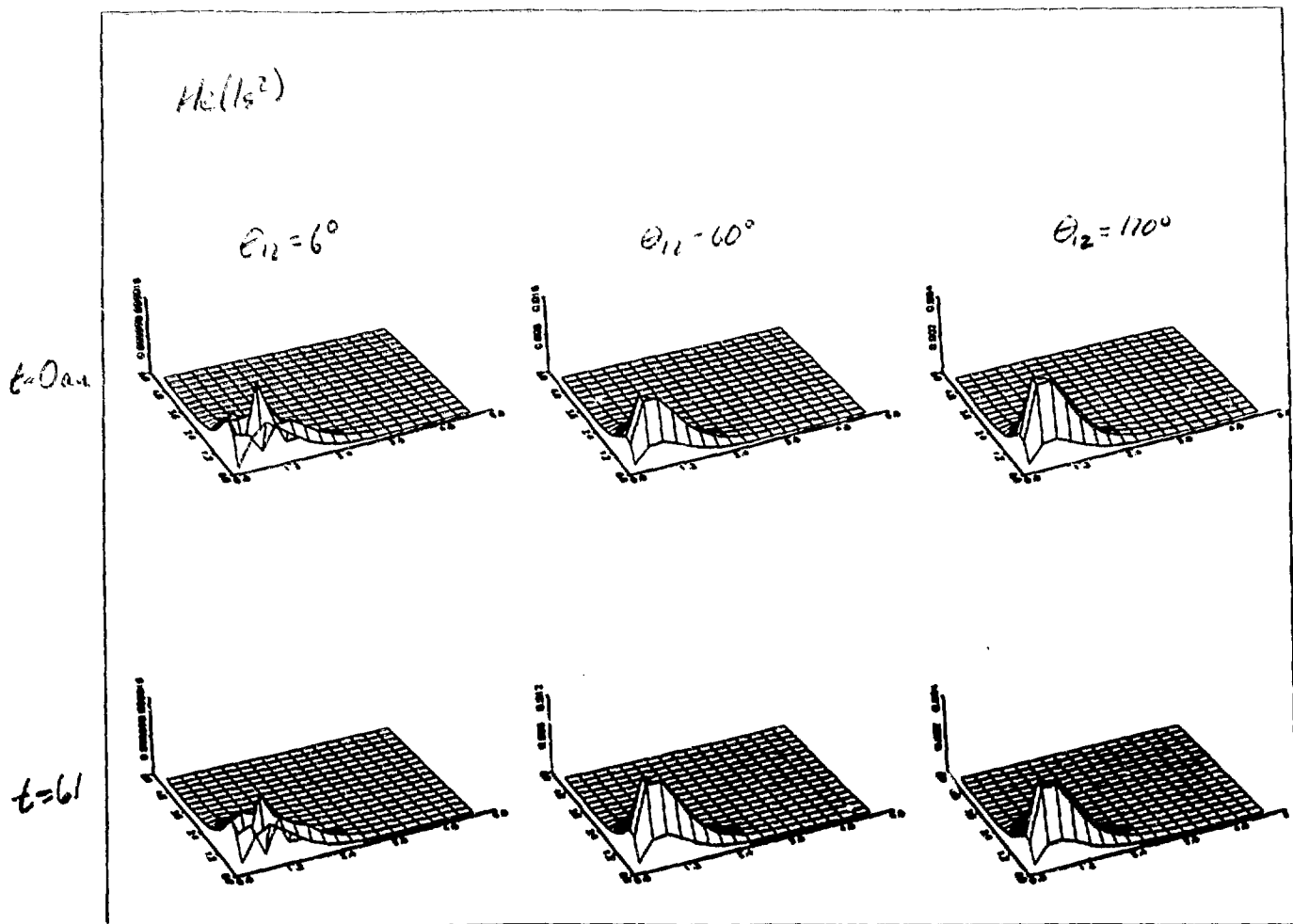


Fig. 5. The ground state of helium, $He(1s^2)$, is depicted for times $t = 0$ and 61 a.u. at three values of θ_{12} , the angle between \vec{r}_1 and \vec{r}_2 . The stationary nature of the state is manifested.

He(1s²)

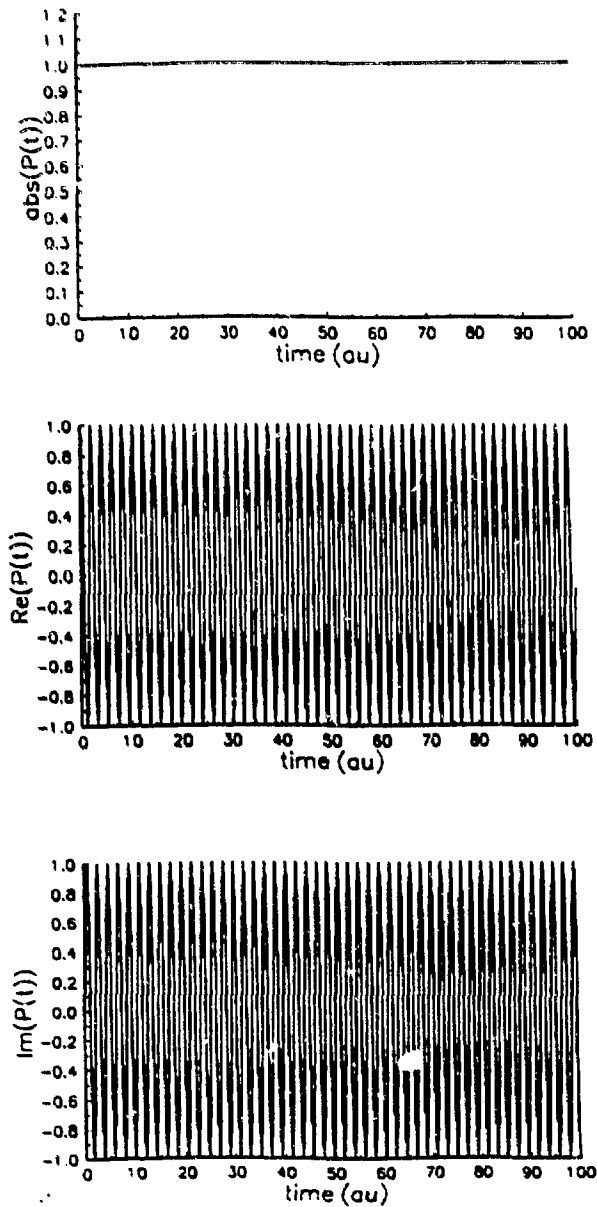


Fig. 6. The square of the correlation function and its real and imaginary parts for the time evolution of the $He(1s^2)$ state, showing the lack of decay of this state.

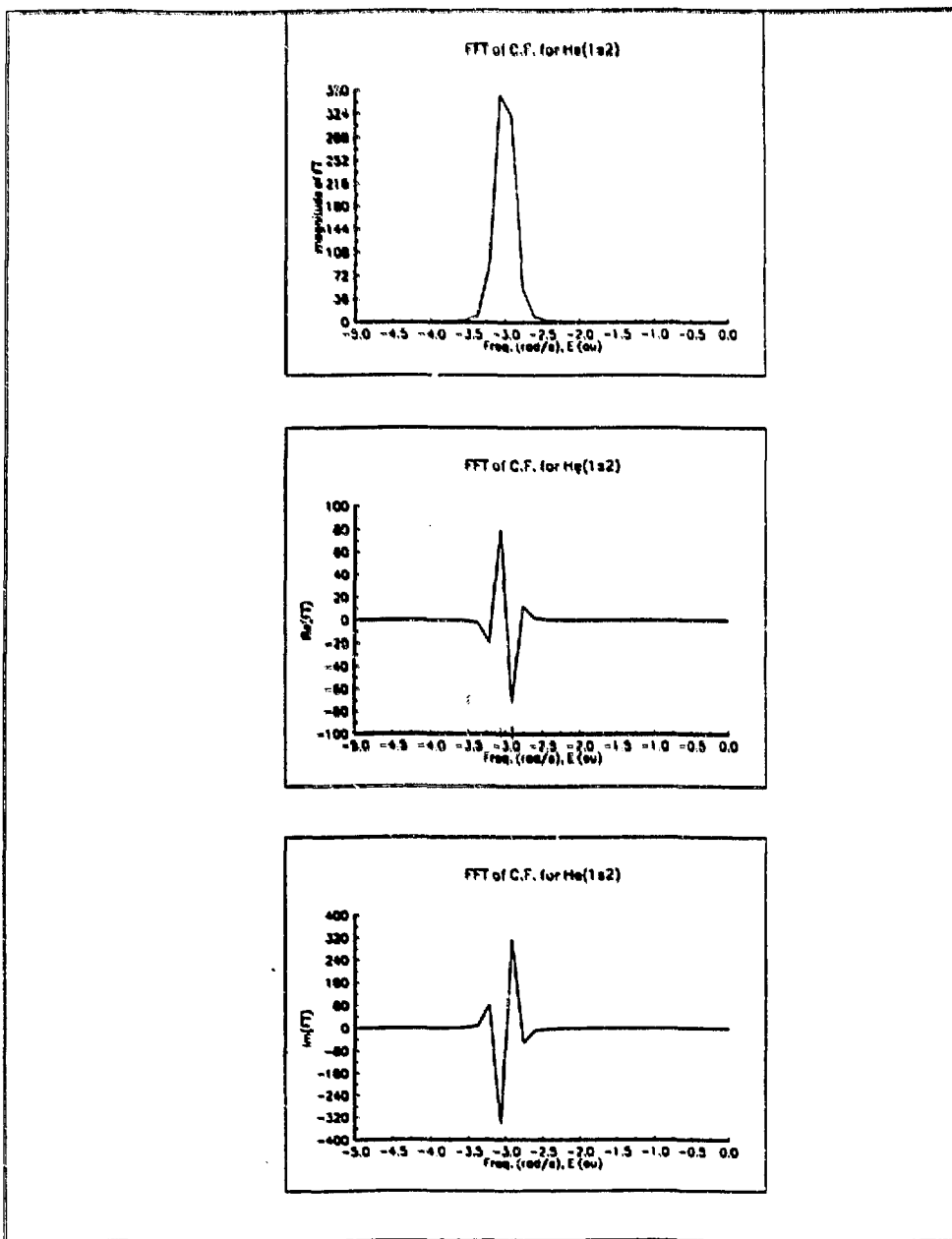


Fig. 7. The magnitude of the Fourier transform of the correlation function and its real and imaginary parts for the $He(1s^2)$ state. Line-shape fitting to the large peak gives an accurate value for the ground state energy eigenvalue for helium.

Time-dependent perturbation theory model

Consider a Hamiltonian which includes a complex absorbing potential (absorb wf at walls, give eigenvalues a width),

$$\mathcal{H} = \mathcal{H}_0 + V + iW = \mathcal{H}_c \quad (1)$$

Assume complete set of states for \mathcal{H}_c

$$\mathcal{H}_c \phi_k = (\mathcal{E}_k - i\gamma_k/2)\phi_k = E_k \phi_k \quad (2)$$

For the full Hamiltonian

$$\mathcal{H}\Psi = i\partial\Psi/\partial t \quad (3)$$

expand

$$\Psi = \sum_k c_k(t)\phi_k e^{-iE_k t} \quad (4)$$

Standard result of time-dependent perturbation theory

$$\dot{c}_n = -i \sum_k c_k(t) V_{nk} e^{i\omega_{nk} t} \quad (5)$$

where

$$V_{nk} = \langle \phi_n | V | \phi_k \rangle \quad (6)$$

$$\omega_{nk} = E_n - E_k \quad (7)$$

1) strong coupling approximation, assume only V_{n0} is important

$$i\dot{c}_n = c_0 V_{n0} e^{i\omega_{n0}t} \quad (1)$$

2) assume $c_0(t)$ is more slowly varying than $e^{i\omega_{n0}t}$ and integrate

$$c_n = c_0 V_{n0} (1 - e^{i\omega_{n0}t}) / \omega_{n0} \quad (2)$$

3) for $t \gg 2/\gamma_k$

$$\dot{c}_0 = e^{-(\Gamma/2 + i\omega_0 - i\delta)t} \quad (3)$$

where

$$\Gamma/2 = \sum_{k \neq 0} (|V_{k0}|^2 \gamma_k / 2) (\omega_{k0}^2 + \gamma_k^2 / 4)^{-1} \quad (4)$$

$$V_{00} = \langle \phi_0 | V | \phi_0 \rangle \quad (5)$$

$$\delta = \sum_{k \neq 0} (|V_{k0}|^2 \omega_{k0}) (\omega_{k0}^2 + \gamma_k^2 / 4)^{-1} \quad (6)$$

4) Correlation function

$$\langle \Psi(t) | \Psi_0 \rangle = \langle \phi_0 | \Psi_0 \rangle e^{-\Gamma t / 2} e^{-i(E_0 + i\omega_0 + \delta)t} \quad (7)$$

$$- e^{-iE_0 t} \sum_{k \neq 0} c_0 V_{k0} \omega_{k0}^{-1} \langle \phi_k | \Psi_0 \rangle \quad (8)$$

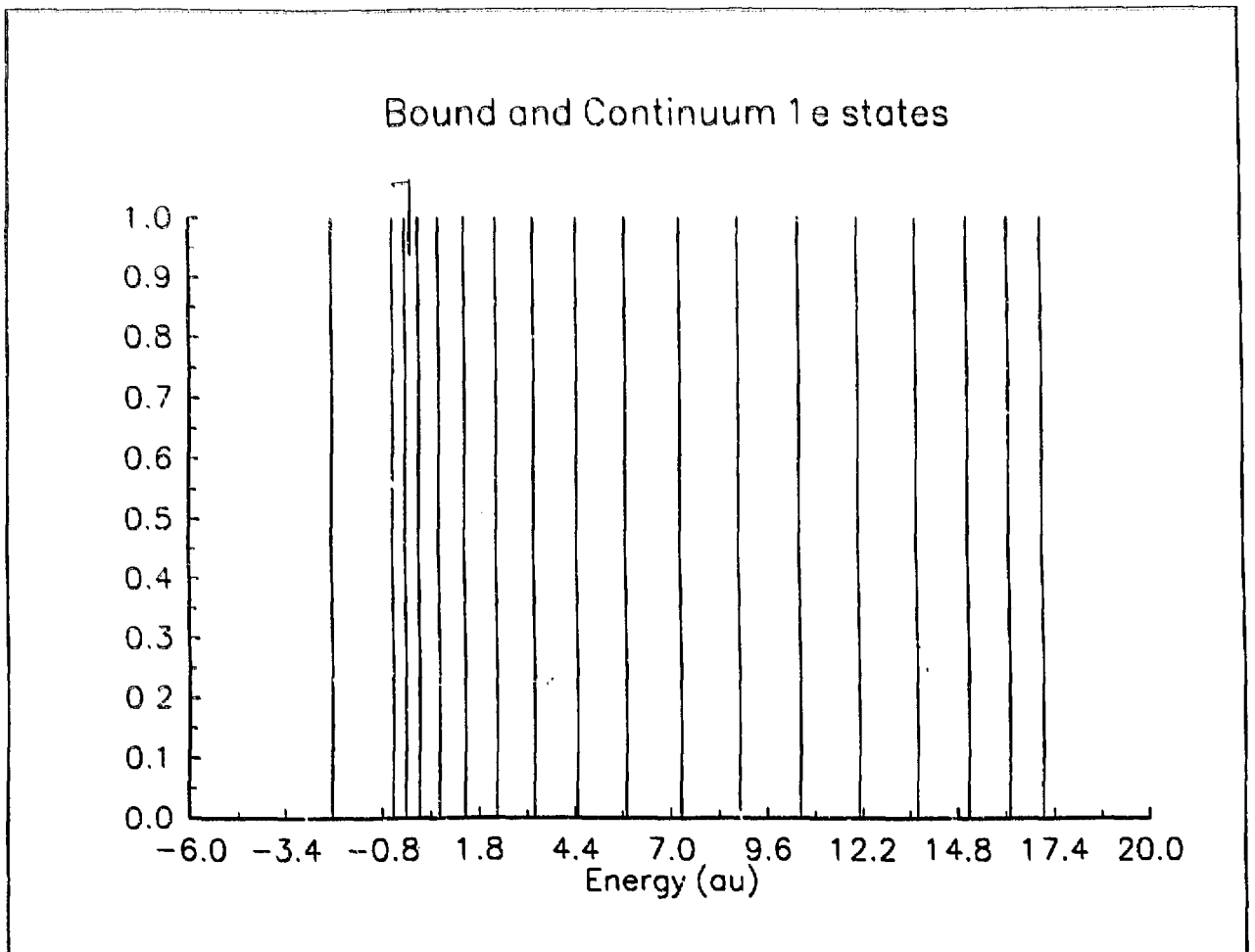


Fig. 8. Spectrum of bound and continuum one electron states obtained without a complex absorbing potential, indicating the discrete nature of the 'continuum' in this finite domain represented on the lattice.

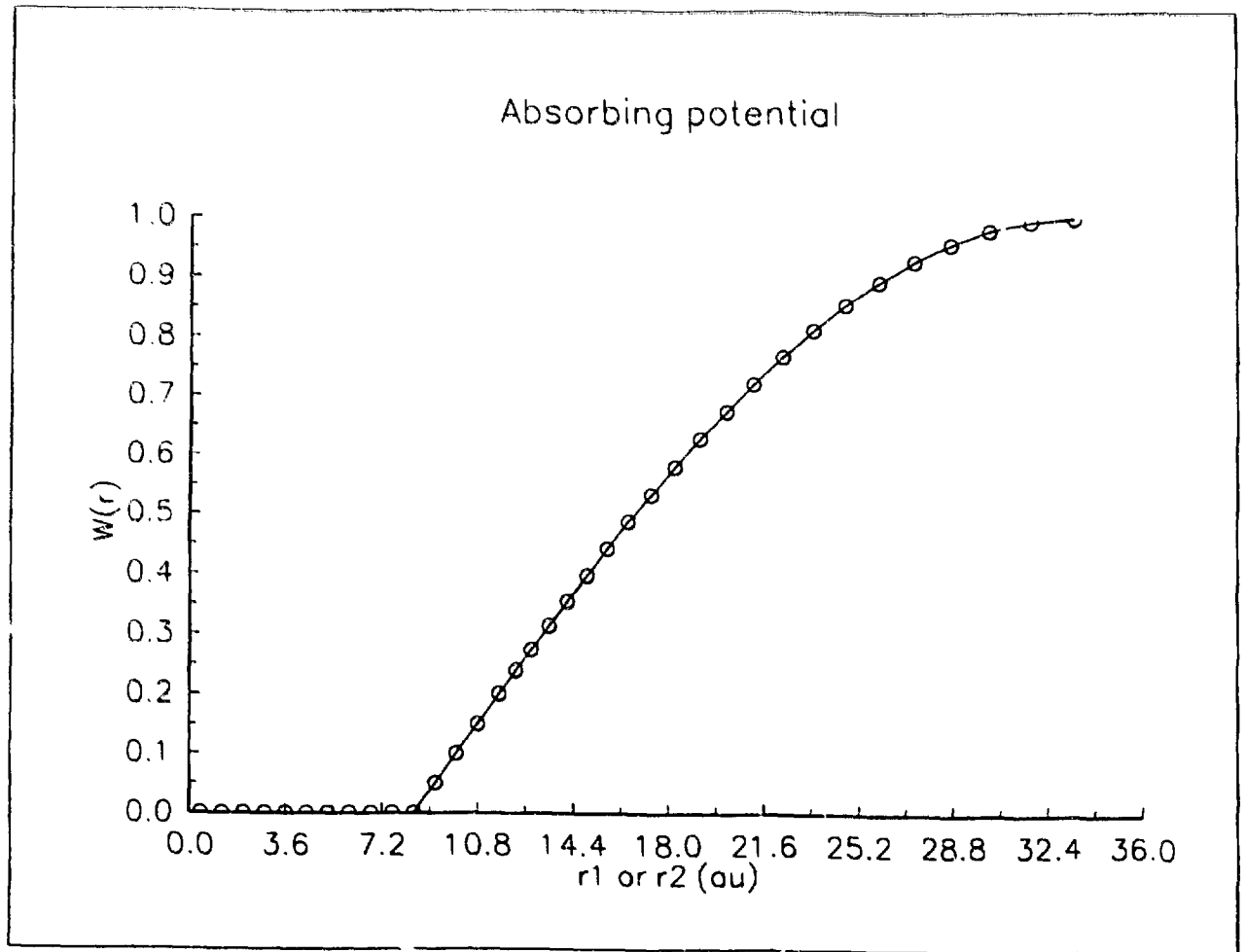


Fig. 9. Displayed is the form of the absorbing potential chosen, illustrating that it is zero within the extent of the initial state and that it then increases for larger values of radial distance. The open circles indicate the positions of the collocation points.

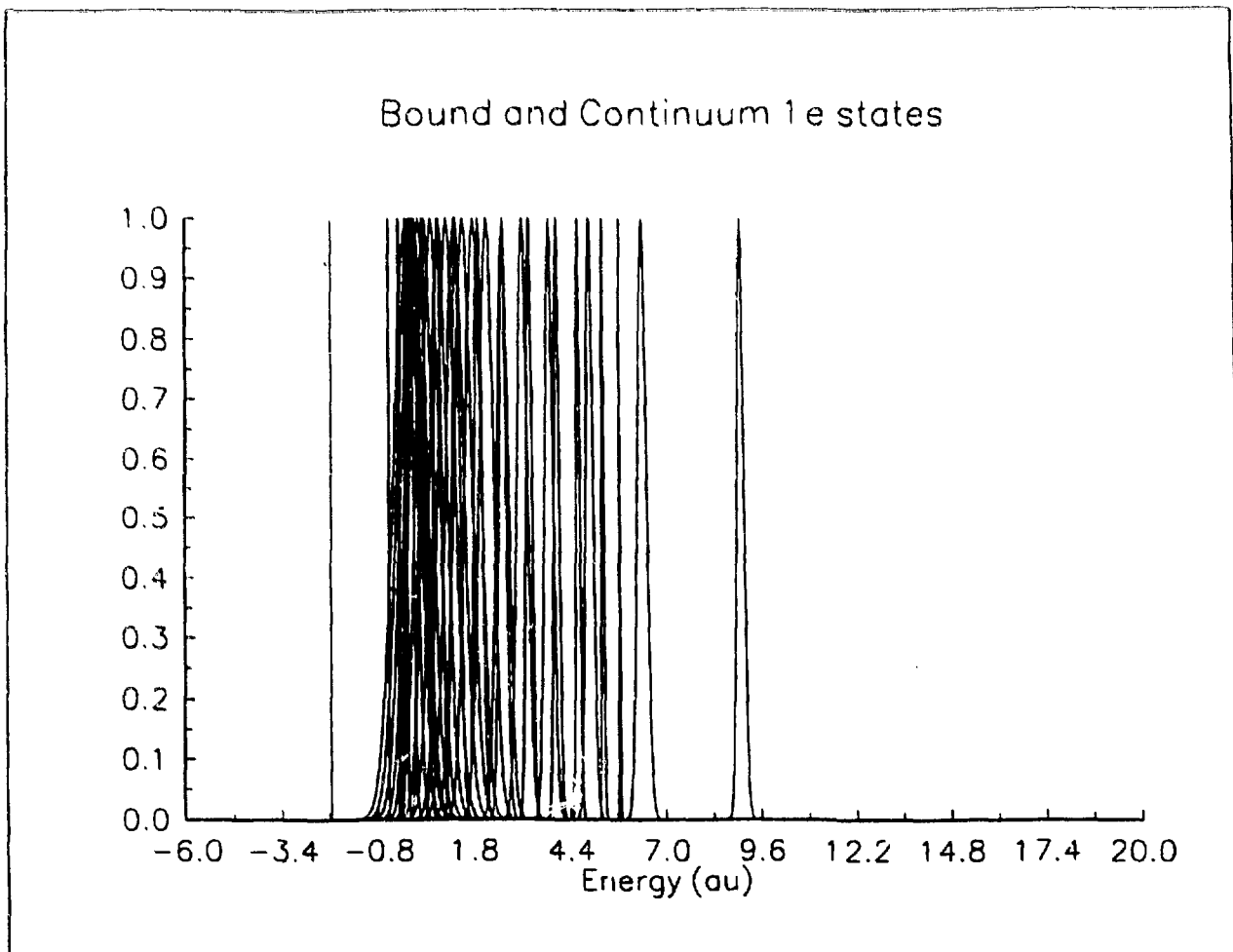


Fig. 10. Spectrum of bound and continuum one electron states obtained with the complex absorbing potential displayed in Fig. 9. Note that the width of the states is such that the continuum is more densely represented.

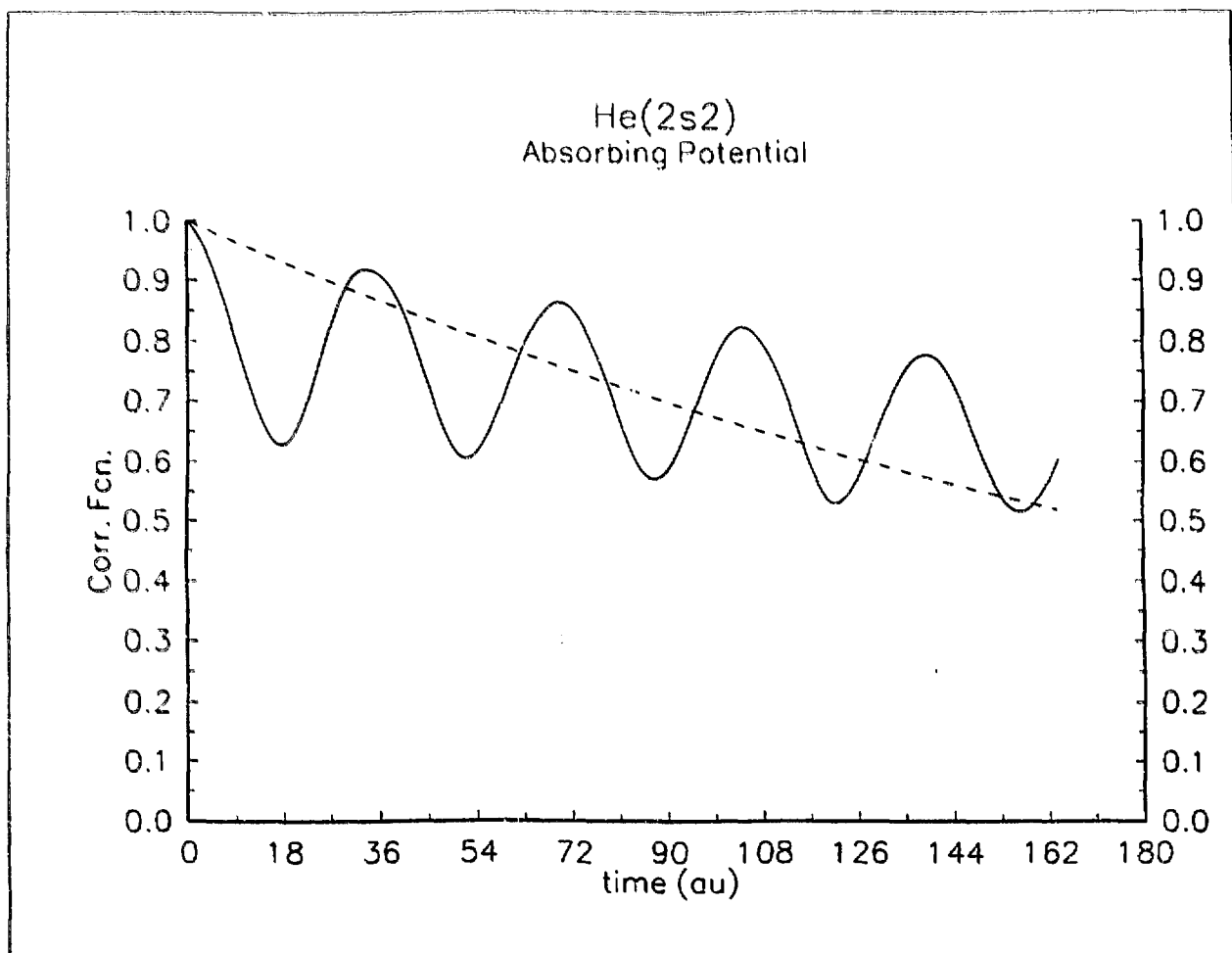


Fig. 11. The correlation function illustrating the decay of the $He(2s^2)$ state when the complex absorbing potential is included so as to provide a good representation of the continuum and prevent the unphysical replenishment of the state from its discrete representation. The dashed curve indicates the expected exponential decay based on the accepted value of the decay constant.