UCRL-JRNL-227046

LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Finite-temperature exchange-correlation theory for dense, partially ionized matter

A. B. Ritchie

January 3, 2007

Physical Review B

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Updated October 14, 2003

Finite-temperature exchange-correlation theory for dense, partially ionized matter

Burke Ritchie

University of California
Lawrence Livermore National Laboratory
Livermore, California 94550

The increased importance of exchange-correlation in dense, partially ionized matter at elevated temperatures is demonstrated for the first time using ab initio theoretical methods. Good agreement with the Kohn-Sham exchange model, as extended to finite temperatures by Gupta and Rajagopal, is obtained for the Be Hugoniot at maximum compression.

Exchange-correlation is achieved by calculating the quantum average of the electron-electron interaction using the spectral solution of the time-dependent Schroedinger equation, which is a superposition of eigenfunctions. The quantum average of the electron-electron interaction has strong temporal fluctuations about a stationary time average. The eigenfuctions calculated in the temporally fluctuating potential are sensibly stationary.

In electron-atom scattering the importance of electron exchange decreases with increasing electron energy [1]. Therefore one might expect exchange to be less important at the elevated temperatures achieved in shock experiments in which solid materials undergo compression and partial to complete ionization. This expectation might be realized but for the compression of the material, which leads to the counter expectation of increased exchange and correlation in the electronic structure of the material due to the close quarters experienced by individual atoms in various stages of ionization. Gupta and Rajagopal [2] addressed this problem using a finite-temperature extension of the zero-temperature Kohn-Sham [3] exchange model and found an analytic limit for high temperatures which is written,

$$V_X = \frac{2T_F}{3T} V_{KS} \ , \qquad (1)$$

where T is the temperature, $V_{KS} = -e^2(\frac{3}{\pi}\rho)^{\frac{1}{3}}$ is the standard Kohn-Sham exchange potential for T = 0, where ρ is the electronic density, and $T_F = \frac{\hbar^2}{2mk_B}(3\pi^2\rho)^{\frac{2}{3}}$ is the Fermi temperature, where k_B is Boltzmann's constant. Remarkably the analytic limit, in which the exchange potential now depends linearly on the density instead of on the one-third power, predicts that the importance of exchange increases with material compression at elevated temperatures if the compression overcomes the temperature in the sense $\frac{2T_F}{3T} > 1$. Quantum self-consistent field calculations [4] have been performed for all temperatures by scaling V_{KS} by the factor $(1+\frac{3T}{2T_F})^{-1}$ which show that compression does indeed overcome temperature at maximum compression such that the material is

predicted to be more compressible than that predicted by using V_{KS} alone (Fig. 1). Greater material compressibility is associated with increased exchange-correlation.

Exchange and correlation refer to the same physical phenomenon: the symmetry of the many-electron Hamiltonian with respect to the permutation of electrons and the exact representation of the electron-electron Coulomb interaction. The two different terms arose in the development of approximation methods in the early history of quantum mechanics when independent-electron methods such as the Hartree and Hartree-Fock methods were used to achieve an approximate energy in which the electron-electron interaction was represented as the interaction of one electron at a time with the average field or "cloud" of all the other electrons. The Hartree-Fock method accounted for electron exchange. The difference between the Hartree-Fock and exact energies became known as the correlation energy.

The use of a symmetrized product of atomic orbitals as a zeroth-order basis became the standard practice, although as discussed by Heisenberg [5] and later by Hartree [6] simple products of orbitals can also be used because, due to the exchange symmetry of the Hamiltonian, permutation symmetry is introduced order by order in a convergent perturbation theory in which the electron-electron interaction is the perturbation. The calculation of the states of He by Riley et al. [7] is an implementation of this principle. The authors use simple products of atomic orbitals as a zeroth-order basis set, and a correlated wave function with the correct permutation symmetry is achieved through the use of high-order perturbation theory.

I return to the use of a simple product of orbitals in this paper. This is a natural step

on solving the time-dependent, independent-electron Schroedinger equation to obtain a spectral representation of the wave function, i. e. a wave function which is a superposition of eigenfunctions [8]. This means that the electron-electron interaction, r_{ij}^{-1}, averaged with respect to the spectral wave function of one of the electrons and expressed as a function of the position of the other, represents the interaction of one electron with the other electron in various stages of excitation and ionization. If r_{ij}^{-1} is averaged with respect to a spectral wave function which spans the entire energy space of either electron i or j, then the exchange-correlation physics of the many-electron problem will have been described. It should be noted that the present theory does not fully account for exchange-correlation because excitations into p, d, etc. orbitals have not been included; this inclusion would entail solving coupled time-dependent radial equations.

The eigenfunction content of the spectral wave function depends on the choice of the wave function at initial time (here a linear combination of orbitals having an analytic variational form). The parameters of the initial wave function are varied to achieve a minimum total energy as calculated from the expectation value of the exact Hamiltonian. This quantity is calculated using the eigenfunctions obtained from a spectral resolution of the spectral wave function – that is from the temporal Fourier transforms of the spectral wave function at the spectral maxima, which are the eigenvalues of the one-electron Hamiltonian in which r_{ij}^{-1} is spectrally averaged. Fig. 2 shows the spectral wave function and the spectrally resolved 1s and 2s eigenfunctions.

Of course the spectrally averaged r_{ij}^{-1}, V_s, oscillates in time, as shown in Fig. 3,

with a mixture of frequencies corresponding to the eigenfunction content in the superposition. Notice that V_s oscillates about a stationary time average. Also notice that r_{ij}^{-1} averaged with respect to the eigenfunctions shows oscillations which are strongly damped with time about a stationary mean; these amplitudes are sufficiently damped by a time of 100 a.u. that they are negligible compared to the amplitudes of V_s. Thus are the eigenfunctions and eigenfunction-averaged variables sensibly stationary or at least quasi-stationary.

Recall that the eigenfunctions are calculated from the spectrum obtained by solving the Schroedinger equation in the the strongly oscillating potential and not from the quasi-stationary potential calculated using the eigenfunctions. The latter procedure would lead back to a Hartree calculation requiring iteration to self consistency and would lose any exchange-correlation effects. This point is illustrated in Fig. 4 which shows the potentials versus r at the maximum time in Fig. 3. Notice that the potentials obtained using the spectral wave function average are less repulsive than that obtained using the eigenfunction average. A net attraction relative to the repulsion caused by the screening of the nuclear charge by the other electrons represents the physical effect of exchange-correlation. Remarkably the divergence for $r < r_{max}$ of the potential obtained using the eigenfunction average (dotted curve) and the potential obtained using the spectral wave function average (solid curve) is a quantitative metric of exchange-correlation in the present calculation.

In the remainder of the paper I will discuss the salient technical details of the calculation and further discussion of the results. I solve the time-dependent radial

Schroedinger equation,

$$i\frac{\partial\psi}{\partial t}=[-\frac{1}{2}(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r})-\frac{4}{r}+3(\frac{1}{r_>}\int_0^r dr'r'^2|\psi|^2+\int_r^\infty dr'r'|\psi|^2)(e^{\frac{\varepsilon}{k_BT}}+1)^{-1}]\psi, \quad (2)$$

where ε is the expectation value of the Hamiltonian given in Eq. (2) and the repulsive electron-electron potential [term multiplied by 3 on the right side of Eq. (2)] is plotted in Figs. 3 and 4. The dependence of the solution one is solving for in Eq. (2) on terms which depend on this solution do not appear to cause any problems in successfully generating the numerical solution and require no iterative scheme as in time-independent quantum theory. The time-dependent solution relaxes rapidly from an initial trial wave function, which is a linear combination of Slater-type orbitals, to its stationary value, as is clear from Fig. (3) in the eigenfunction representation of r_{ij}^{-1}. The electronic density is normalized using the standard relation,

$$4\pi\int_0^R drr^2 2[|\psi_{1s}|^2(e^{\frac{E_{1s}-\mu}{k_BT}}+1)^{-1}+|\psi_{2s}|^2(e^{\frac{E_{2s}-\mu}{k_BT}}+1)^{-1}+\rho_c]=4 \qquad (3a)$$

$$\rho_c=\frac{(2m/\hbar^2)^{\frac{3}{2}}}{\pi}\int_0^\infty dEE^{\frac{1}{2}}|\psi_E|^2(e^{\frac{E-\mu}{k_BT}}+1)^{-1}, \qquad (3b)$$

where Eq. (3a) contains the 1s and 2s spectrally resolved eigenvalues and eigenfunctions [8] and the continuum-orbital density ρ_c. R is the ion-sphere radius and μ is the chemical potential. The continuum orbitals are calculated by solving the radial time-dependent Schroedinger equation using the potential used in Eq. (2) and with starting functions equal to spherical Bessel functions for partial waves $\ell=0,1.....10$ and at energies E from zero to nine times the temperature on an energy grid containing eighteen points.

The Schroedinger equations are solved within the ion-sphere using the Crank-

Nicolson implicit scheme with boundary conditions of constant solution and zero slope at the ion-sphere radius. The numbers of grid points used are 512 for r and 10000 for t for maximum times of 10 or 20 a.u. Fewer grid points could probably be used to achieve comparable accuracy, especially for Z=4, but I have not optimized the calculations for computational efficiency since they are cheap per parameter set on the Livermore machines.

As mentioned earlier the eigenfunctions (Fig. 2) are obtained from the temporal Fourier transform of ψ at the spectral maxima, which are the eigenenergies, as discussed in [8]. These eigenfunctions are used to calculate the total energy as the expectation value of the exact Hamiltonian (making sure not to include any self-interaction terms). The pressure is calculated from the generalized virial theorem. Tables of energies and pressures versus density for temperatures from room temperature to 1 keV are constructed, and the Hugoniot is calculated by interpolation of the tables to solve the Rankine-Hugoniot equation. Inevitably the tables can contain some numerical noise, especially at low temperatures, whose source is probably the use of a single set of initial solution parameters over the entire T, ρ space instead of individually optimizing the calculation at each T, ρ point For example the effect of this numerical noise is evident in the sharp structure in the Hugoniot near 5.5 g/cm^3.

The principal result of this calculation is given in Fig. 1. All theories use the ideal gas law for the ion motion. The Hugoniot of the present theory agrees well at maximum compression with the Gupta-Rajagopal [2] temperature-dependent exchange model, as implemented in the Purgatorio code [4]. The latter model is in good agreement with the

finite-temperature exchange-correlation model [13]; however it agrees poorly with the present results, with the zero-temperature exchange model, and with the zero-temperature exchange-correlation model [13] at intermediate temperatures. The results of [13] have also been presented in comparison with the results of other models in another publication [14]

The tendency of the present theory to overshoot the experimental data in the low-temperature regime is sensitive to the initial parameter set used; however the increased compressibility of the present Hugoniot in the high-temperature regime at maximum compression is robust and appears to be insensitive to the starting parameters.

In summary the present ab initio independent-electron theory appears to capture much of the exchange-correlation in an atom by a quantum average of the electron-electron interaction with respect to a spectral wave function electronic density rather than an eigenfunction electronic density. The spectral wave function is a superposition of eigenfunctions and thus spans the energy space of a one-electron Hamiltonian, which is necessary to describe the many-electron physics of exchange and correlation.

All of the theories confirm the Gupta-Rajagopal [2] prediction of the increased importance of exchange for a compressed material at elevated temperatures. There is much disagreement among the various theories in the intermediate-temperature regime which requires elucidation by further theoretical work or by experiment.

Acknowledgements. The author is grateful to T. Scott Carman for support of this research. He wishes to thank Stephanie Hansen, Phil Stern, Brian Wilson, and William Isaacs for making the Purgatorio results available to him. He also wishes to thank Charles Weatherford, Jerry Kerley and Senor Balazs Rozsnyai for helpful discussion. This work was performed under the auspices of the U. S. Department of Energy by the University of California under Contract No. W-7405-ENG-48.

References

1. Merle E. Riley and Donald G. Truhlar, J Chem. Phys. **63**, 2182 (1975)

2. U. Gupta and A. K. Rajagopal, Phys. Rev. A **21**, 2064 (1980)

3. W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965)

4. D. A. Liberman, Phys. Rev. B **20**, 4981 (1979); B. Wilson, V. Sonnad, P. Sterne, and W. Isaacs, J. Quantitative Spectroscopy and Radiative Transfer, **99**, 658 (2006)

5. W. Heisenberg, Z. Physik **39**, 499 (1927)

6. D. R. Hartree, Proc. Cambridge Phil. Soc. **26**, 89 (1928)

7. Merle E. Riley, J. M. Schulman, and J. L. Musher, Phys. Rev. A **5**, 2255 (1972)

8. M, D. Feit, J. A. Fleck, and A. Steiger, J. Computational Phys.**47**, 412 (1982)

9. S. P. Marsh, LASL Hugoniot Data, University of California Press, Berkeley, 1980

10. W. M. Isbell, F. H. Shipman, A. H. Jones, General Motors Corporation Materials Science Laboratory Report MSL-68-13, 1968

11. W. J. Nellis, J. A. Moriarty, A. C. Mitchell, and N. H. Holmes, J. Appl. Phys. **82**, 2225 (1997)

12. C. E. Ragan III, Phys. Rev. A **25**, 3360 (1982)

13. M. P. Surh, T. W. Barbee III, and L. H. Yang, Phys. Rev. Lett. **86**, 5958 (2001)

14. B. Rozsnyai, J. R. Albritton, D. A. Young, V. N. Sonnad, and D. A. Liberman, Phys. Lett. A **291**, 226 (2001)

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Figure Captions

Figure 1. Shock Hugoniots for Be. Solid curve: present theory. Long-dashed curve: Purgatorio with zero-temperature exchange. Short-dashed curve: Purgatorio with finite-temperature exchange. + data points: experiment [9-12]. Triangles: T = 0 exchange-correlation theory [13]. Stars: Finite-temperature exchange-correlation theory [13].

Figure 2. Wave functions at maximum time and at room temperature and 0.1 g/cm^3. Solid curve: spectral wave function ψ. Long-dashed curve: 1s eigenfunction ψ_{1s}. Short-dashed curve: 2s eigenfunction ψ_{2s}. Each wave function has unit normalization within the ion-sphere.

Figure 3. Quantum averages of the electron-electron interaction near the point nucleus versus time. Lower curves: r_{ij}^{-1} averaged with respect to the distribution $3|\psi|^2$ and its time average. Upper curve: r_{ij}^{-1} averaged with respect to the distribution $2|\psi_{1s}|^2 + 2|\psi_{2s}|^2$.

Figure 4. Quantum averages of the electron-electron interaction versus r at the maximum time of Fig. 3. Long dashed curve: r_{ij}^{-1} averaged with respect to the distribution $3|\psi|^2$. Short-dashed curve: r_{ij}^{-1} averaged with respect to the distribution $2|\psi_{1s}|^2 + 2|\psi_{2s}|^2$. Solid curve: r_{ij}^{-1} averaged with respect to the distribution $4|\psi|^2$. Notice that the various curves are equal to n/r at the ion-sphere radius, where n is the number of electrons.

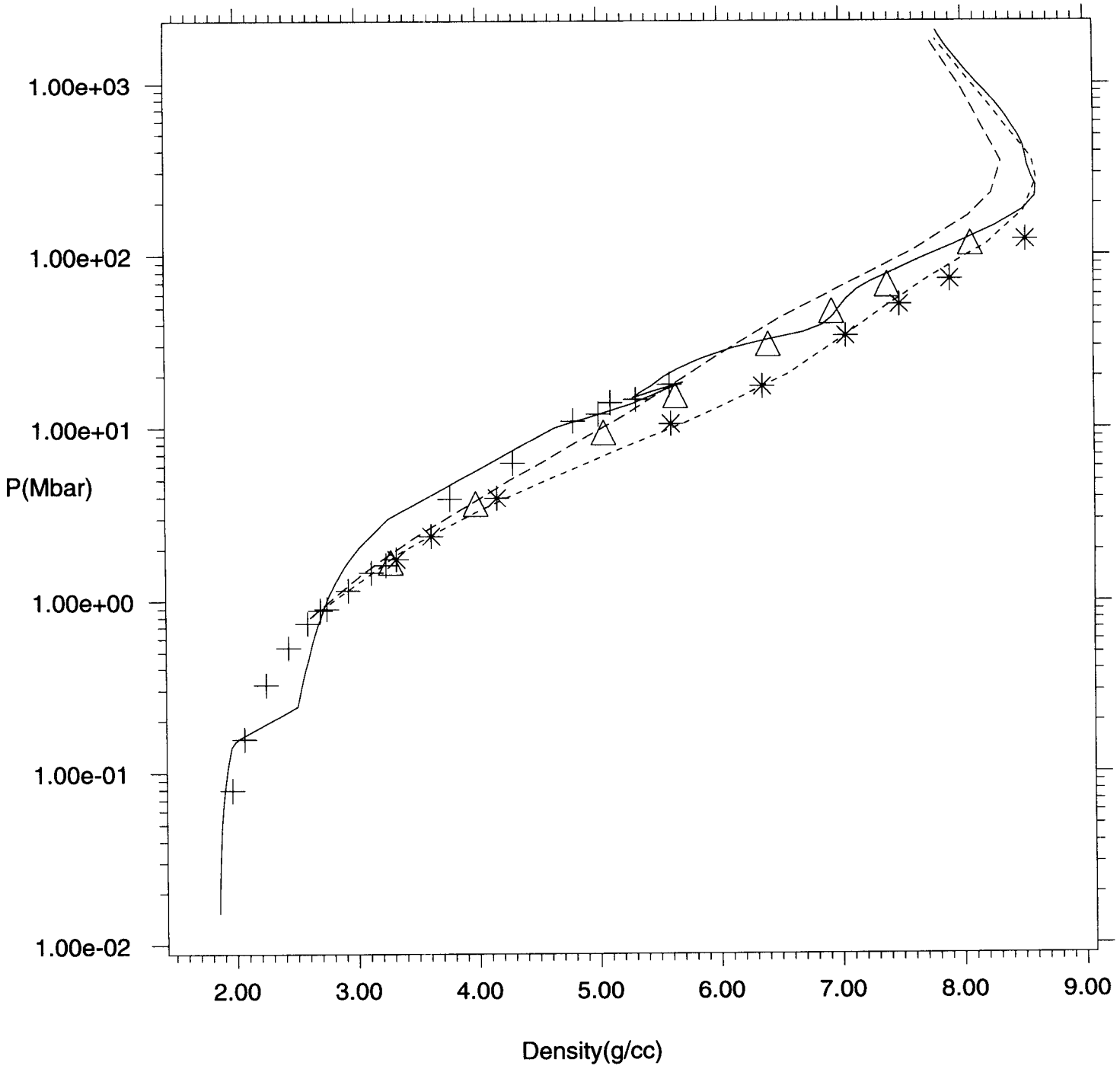
1.00e+03
1.00e+02
1.00e+01
P(Mbar)
1.00e+00
1.00e-01
1.00e-02
2.00
3.00
4.00
5.00
6.00
7.00
8.00
9.00
Density(g/cc)

Fig. 1

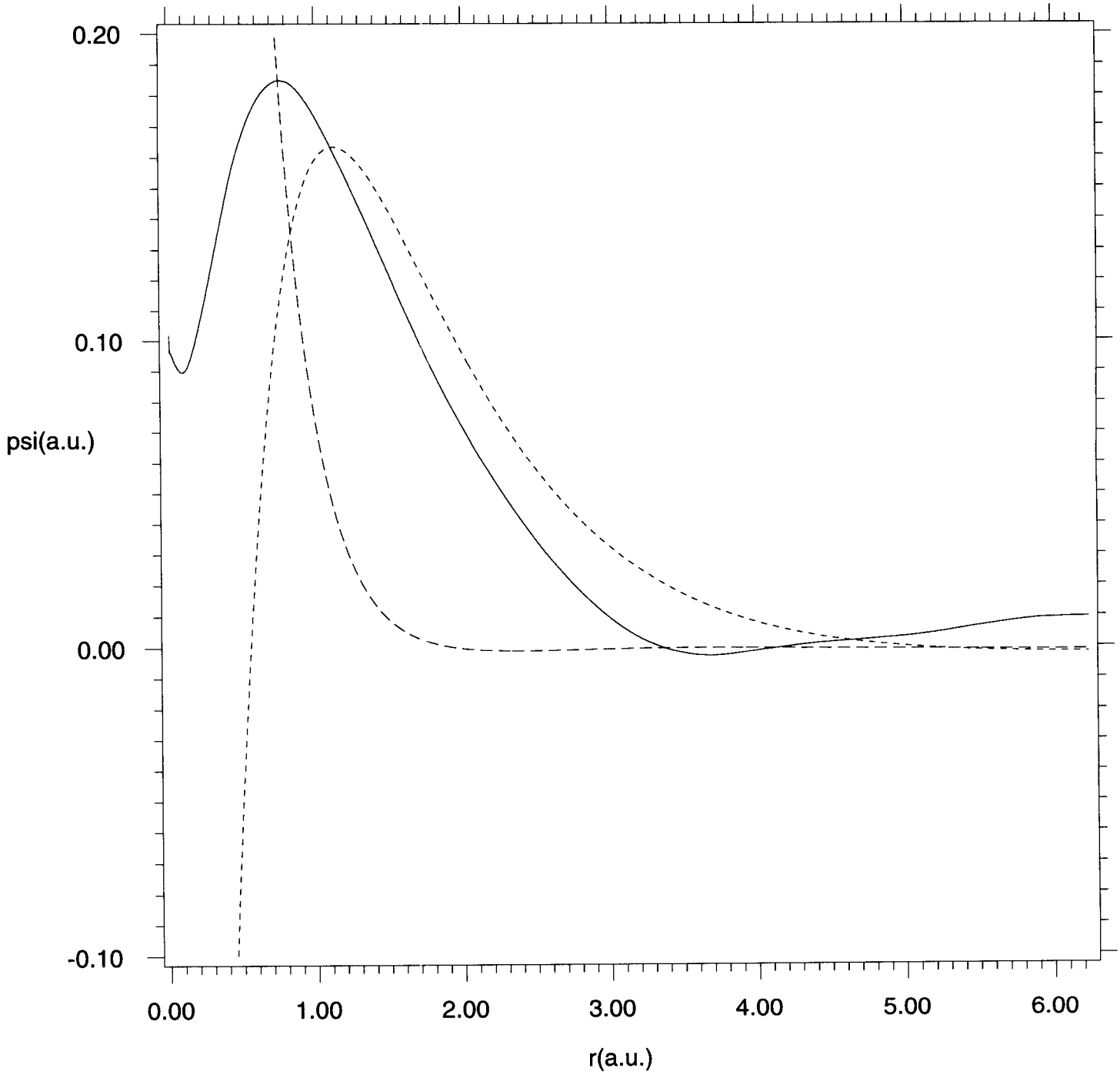

Fig. 2

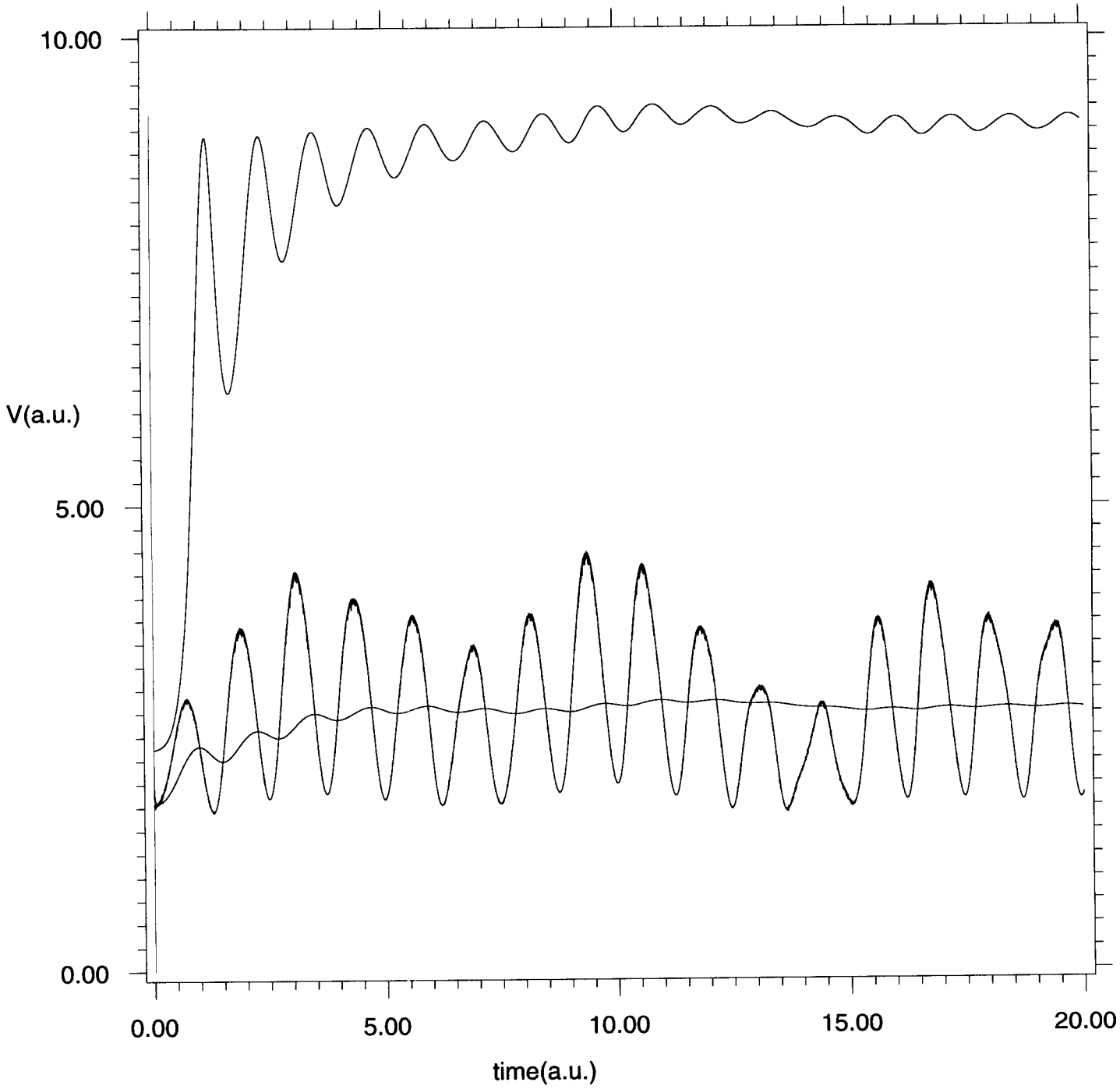

Fig. 3

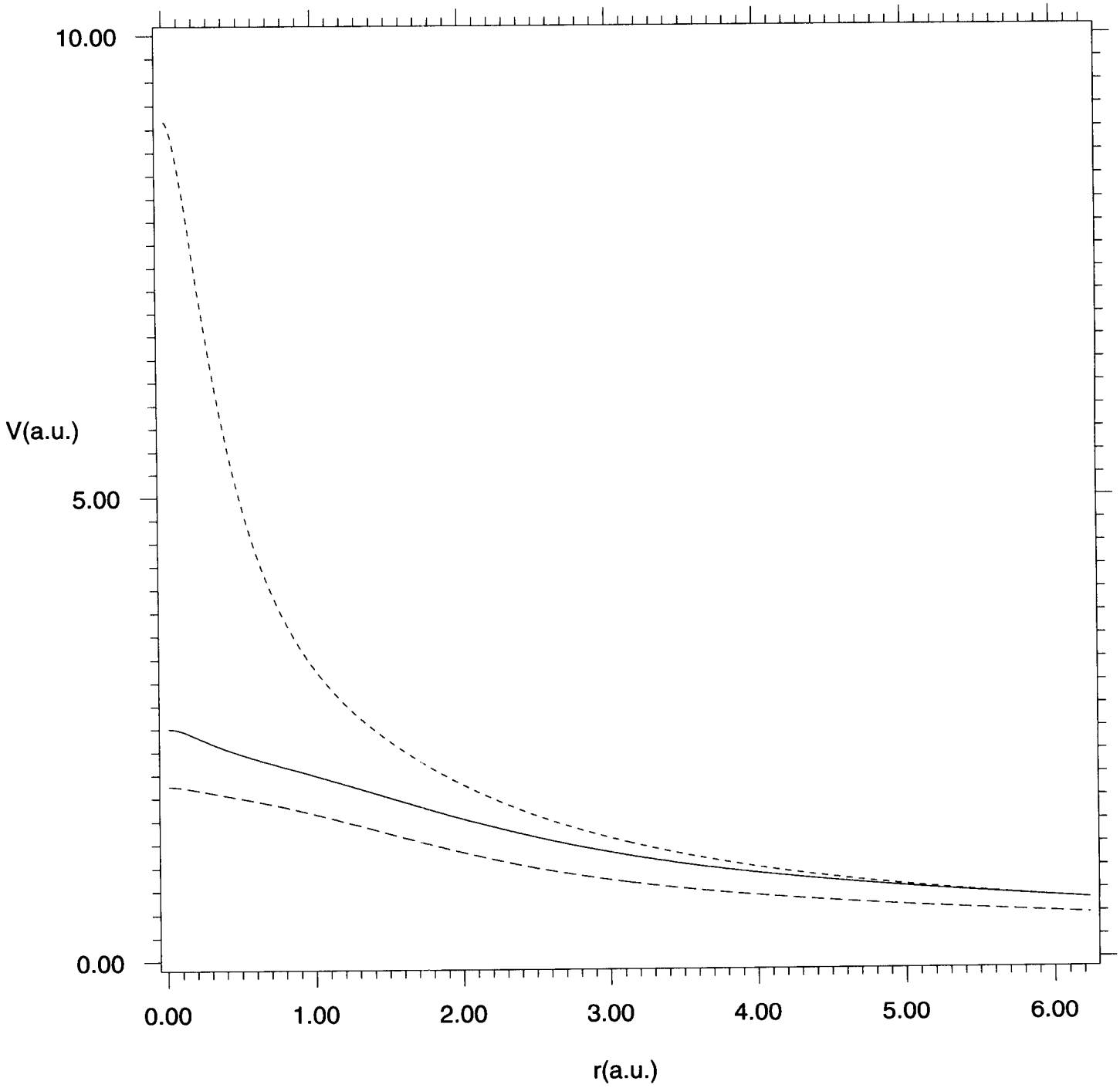

Fig. 4