Doped ^{3}He clusters: A systematic quantum chemistry approach to fermionic nuclear wavefunctions and energies

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Abstract

A novel approach for calculating nuclear wavefunctions and energies of ^{3}He clusters doped with an atomic or molecular impurity is developed. It adopts the systematic and well developed methodology of quantum chemistry employing an analogy between electrons bound by Coulomb forces to the nuclei and fermionic ^{3}He atoms clustered around a dopant species. The differences primarily concern the different shapes of the helium-helium and helium-impurity potentials and the larger mass of the ^{3}He atom, as compared to electronic structure problems. A new integral evaluation procedure is outlined, as well as the necessary modifications to electronic structure codes. Tests against numerically exact calculations for Imp-^{3}He (Imp = Ne, Ar, Kr, Xe, and SF_6) complexes show that a modest set of 15 basis functions provides accurate and converged results. Calculations for the lowest triplet state of the $SF_6(^3He)_2$

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cluster, where fermionic statistics comes into play in the orbital part of the helium nuclear wavefunction, are presented. The triplet state is bound by 22 μhartree with respect to dissociation into ^{3}He + SF_6-^{3}He. The applicability of the new method to larger systems is discussed.

I. INTRODUCTION

Helium possesses two stable isotopes — ^{4}He and ^{3}He. The large amount of experimental and theoretical studies concerning pure or doped nanodroplets formed by bosonic ^{4}He has been reviewed recently, e.g. in the focus article by Kwon *et al.*[1] In that paper it is mentioned, within a prognosis for future research directions, that the behavior of molecules solvated in clusters of fermionic ^{3}He is "of considerable interest". Indeed, ^{3}He clusters differ significantly from those composed of the ^{4}He isotope due to the lower mass and particularly due to the fermionic statistics of the former systems. Most notably, while ^{4}He nanodroplets formed at 0.38 K are superfluid, those containing ^{3}He, even though formed at a lower temperature of 0.15 K, do not exhibit superfluidity.[2–3] Thus, these systems represent a unique laboratory for studying solvation in *bosonic and superfluid* vs. *fermionic and non-superfluid* quantum solvents.

Pure ^{3}He clusters are inherently difficult to prepare. This is due to the fact that, unlike the case of ^{4}He, the dimer and even larger aggregates are not bound (the smallest bound ^{3}He cluster is estimated to have 35 atoms[4]). Thus, it is virtually impossible to obtain these clusters by condensation in a supersonic jet. Nevertheless, numerous theoretical studies have addressed questions concerning the structure and stability of pure ^{3}He clusters containing tens to hundreds of atoms.[4–12] Different approaches ranging from variational Monte Carlo[11] to local[10,12] and non-local[6] density functional methods, and to a configuration interaction with Jastrow-type short-range correlations[4–5] have been applied to fermionic helium clusters, the central question being the existence of a shell structure and magic numbers.

A practical way of experimentally preparing ^{3}He clusters is to allow them to condense, after supersonic expansion into the vacuum, at an atomic or molecular impurity, as in recent experiments on a single OCS or SF_6 molecule embedded in pure ^{3}He or in mixed ^{3}He-^{4}He clusters.[2,13] In addition to being the nucleation center, the dopant molecule serves as a spectroscopic probe that allows to quantitatively address two classes of questions. The first one concerns the structure of the quantum solvent around the dopant molecule, while the second class concerns perturbations in the solute quantum states (particularly its rotational levels) by solvation.[2] In direct connection with the above experiments, calculations employing the finite-range density functional method have been applied to pure ^{3}He and mixed ^{3}He-^{4}He clusters doped with SF_6 or xenon.[14–15] These calculations explored the structure of the solvation shells, showing (in agreement with experiment[2]) that ^{4}He tends to replace ^{3}He in the vicinity of the dopant species.

An accurate description of pure or doped fermionic ^{3}He clusters is a major methodological challenge. While diffusion and path integral Monte Carlo methods represent the state-of-the-art for bosonic ^{4}He nanodroplets,[1] extension of these techniques to fermionic systems is highly non-trivial due to the notorious sign problem occuring for wavefunctions possessing a nodal structure.[11,16] Current implementations of alternative approaches based on density functional theory[6,14–15] or on Slater determinants[4–5] involve to a certain extent empirical *ad hoc* assumptions, e.g., in the parameterization of the density functional, in the functional form of orbitals composing the Slater determinants, or of the Jastrow term.

The principal goal of the present study is to develop a systematic first principle approach to calculations of the ground and excited nuclear wavefunctions and energies of doped ^{3}He clusters. The basic idea is to employ the well developed machinery of *ab initio* quantum chemistry,[17–18] exploiting the analogies between: (i) the two the fermions, i.e., an electron and a ^{3}He atom; and (ii) the nuclei in electronic structure problems and a dopant atom or molecule in the present systems, both of which representing sources of the external potential. As the first application of the method, the question about *high-spin*, i.e., triplet in case of two ^{3}He atoms, states stability is addressed. We have found that the lowest triplet state of SF_6-(^{3}He)$_2$ is bound by 22 μhartree with respect to dissociation into ^{3}He + SF_6-^{3}He.

In the following section the novel theoretical approach is outlined. In Section III, results for small ^{3}He clusters doped with heavier rare gas atoms and the SF_6 molecule are presented and discussed. Finally, Section IV contains concluding remarks.

II. THEORETICAL APPROACH

As mentioned in the previous Section, the present theoretical approach is based on similarities between electronic structure problems and many-body nuclear wavefunctions of doped fermionic ^{3}He clusters. Let us explore in more detail this analogy. Since both electrons and ^{3}He atoms are fermions, the whole formalism of *ab initio* electronic structure theory[18] can be adopted in a relatively straightforward way, and one can follow a well established hierarchy of approximations to the exact wavefunction. The series of wavefunctions of increasing complexity[19] typically start from the mean-field Hartree-Fock solution, and proceed to correlated approaches. One of the keys to the success of post-Hartree-Fock methods, such as Möller-Plesset perturbation series, or coupled clusters, is the fact that the mean-field Hartree-Fock solution is usually already a very good first approximation. This in turn is caused by the presence of a strong external force exerted by the nuclei, which contributes to the one-particle part of the total Hamiltonian. In pure ^{3}He nanodroplets there is no such external field and, consequently, Hartree-Fock theory fails to describe the binding. However, in doped clusters, which are at present the only experimentally accessible systems of this type, an external field is created by the dopant atom or molecule. Since for any dopant species the solute-helium interaction is stronger than that between helium atoms, this field is relatively strong, suggesting that the mean-field approach should be a reasonable starting approximation. Moreover, all closed shell atoms and molecules tend to solvate in the center of the helium nanodroplet,[1,13] thus creating a very good analogy to a central nucleus surrounded by electrons. To summarize at this point, in the novel approach presented in this paper, the ^{3}He atoms surrounding an impurity are treated in a similar way to electrons around a nucleus in electronic structure calculations.

Clearly, despite the similarities, there are also notable differences between an electron and a ^{3}He atom, which have to be accounted for. First comes the question of the validity of the Born-Oppenheimer separation between electronic and nuclear motions as compared to those of the helium atom and the impurity in the present case. Although the heavyto-light particle mass ratio is less favorable in the present systems, the Born-Oppenheimer approximation has been successfully applied to ^{3}He clusters doped with SF_6 or xenon.[14–15] We demonstrate in the next Section that accurate results are obtained if the atomic mass of the impurity is at least an order of magnitude larger than that of ^{3}He (note that all the experimental systems studied so far fall into this category). For lighter impurities, the Born-Oppenheimer approximation is less satisfactory, but as we show in Section III, a simple diagonal non-adiabatic correction[20] can to a large extent rectify the problem.

Another major difference between the present problem and that of electronic structure lies in the interaction potential. While in the latter case strong Coulomb interactions come into play, weak van der Waals forces cause binding in the former case. Also, while the electron-electron interaction is always repulsive and electron-nucleus interaction is always attractive, both helium-helium and helium-impurity potentials exhibit strong repulsion at short separations and weak attraction at larger separations. This has direct implications to the structural and energetic properties of the present systems, concerning, for example, closures of quantum shells and occurrence of magic-number cluster sizes.

From a more technical point of view, several modifications of the *ab initio* codes have to be implemented before their application to doped ^{3}He clusters. Beyond the trivial fact that the mass of the fermionic particles has to be increased appropriately, more elaborate changes concern basis set construction and evaluation of integrals. To represent the ^{3}He nuclear orbitals (i.e. one-particle wavefunctions), we have employed, as in most electronic structure calculations, an expansion over Gaussian basis functions. These Gaussians are centered at the dopant moiety. Since ^{3}He nuclear wavefunctions in doped nanodroplets are expected to have a rather diffuse character and a much smaller spatial separation between quantum shells than electrons in atoms, we have constructed the basis set following the standard procedure for diffuse basis sets generation in *ab initio* calculations. Namely, we have used an even-tempered sequence of s and p functions with the nth exponent α_n given by a geometric series:[21] $\alpha_n = \alpha_1/g^{n-1}$. Therefore, for each angular momentum present in the basis, there are two adjustable parameters, α_1 and g. We have obtained the values of the largest exponent α_1 and the geometric factor g by optimizing the energy of the Imp-^{3}He complex for the series Imp = Ne, Ar, Kr, Xe, and SF_6. It is satisfying that: (i) a single set of parameters works equally well for all for rare gas impurities (for SF_6 a smaller value of the largest exponent has been employed); and (ii) no more than 15 s functions are necessary to obtain converged energies. These energies differ by less than 1 % (less than 5 % in the case of the SF_6 dopant) from the numerically exact values, which we have obtained by solving the one-dimensional vibrational Schrödinger equation (setting the mass of the impurity to infinity) by imaginary time propagation[22] on an equidistant grid of 512 points. Finally, for larger complexes, we have reoptimized the basis set with respect to the Hartree-Fock energies, which lead only to minor modifications of the above basis sets.

For the Imp–He and He–He interactions we have employed the accurate and widely used HFD-B pair potentials.[23–25] For the sake of simplicity, we have employed an isotropic, i.e., spherically averaged, potential for the Imp-He interaction.[25] In order to facilitate the evaluation of integrals, we have expanded the above pair potentials into series of Gaussian functions. We have found it useful to expand the repulsive and attractive parts of the potentials separately. Since the repulsive part of HFD-B-type potentials is a product of a Gaussian and an exponential function, it is possible to employ a previously developed accurate expansion of an exponential Slater function into 12 Gaussians.[26] The attractive parts of all potentials are represented accurately by expansions into 30 even-tempered Gaussians with the largest exponent α_1=10 au^{-2}, and the geometric factor g=1.3. The corresponding coefficients have been obtained by linear least-square fitting[27] to the particular pair potential. By numerically exact calculations on the Imp-^{3}He clusters, we have verified that these expansions do not introduce any additional appreciable error into the calculations. Using the above Gaussian expansion of the nuclear wavefunctions and interaction potentials, all the overlap, one-particle (i.e. kinetic energy and Imp-^{3}He interaction), and two-particle (i.e. ^{3}He-^{3}He interaction) integrals can be evaluated analytically.[28–29]

The integral evaluation program was linked to the coupled-cluster codes of the Q-Chem electronic structure program.[30] In addition, we have used the input-output library and input parser of the PSI electronic structure program.[31] An integral transformation module and a simple program for self-consistent field calculations have been written using the C++ tensor library for coupled-cluster calculations.[32] Thus, the current version of the program is capable of performing Hartree-Fock, MP2, coupled-cluster with single and double substitutions (CCSD),[33] and optimized-orbitals coupled-cluster doubles (OO-CCD)[33–35] calculations for doped ^{3}He clusters. Moreover, configuration interaction singles, and equation-of-motion OO-CCD[36] calculations can be employed for calculations of the excited states. Last (but not least) is the capability of carring out equation-of-motion spin-flip (EOM-SF)[37] calculations, which is very useful for heavily-correlated systems. Additional details, as well as programmable expressions for integral evaluation, will be provided in a subsequent publication.[38]

III. RESULTS AND DISCUSSION

As a first benchmark, useful also for basis set optimization, we have performed calculations for five Imp-^{3}He (Imp = Ne, Ar, Kr, Xe, and SF_6) systems. The results are summarized in Table I and in Fig. 1. We have found that a single set of 15 even-tempered s-functions with the largest exponent of 1.7 au^{-2} and a geometric factor of 1.35 provides accurate and converged results for all four systems containing a rare gas impurity. For SF_6, the best results are obtained with the same geometric factor but with a more diffuse basis, i.e., with α_1=1.3 au^{-2}. Table I demonstrates the very good agreement between the present energies and numerically exact results employing the full mass of the ^{3}He atom (i.e., assuming infinite mass of the impurity). We have found that for SF_6 the convergence of the results with the basis set size is slower than for rare gas dimers. For example, the difference between the best result with 15 basis functions and the exact result is 5% for SF_6, while for rare gases a basis set of the same size is capable of reproducing the exact value within 1% error. This is because the stronger SF_6-^{3}He interaction results in a more localized nuclear wavefunction. The performance of the impurity-centered Gaussian basis set becomes slightly inferior as the wavefunction becomes more localized. Note also that the energies in Table I correspond to the specific choices of the He-He and Imp-He potentials, and marginally different results would be obtained with other potentials.[39–40]

Table I also demonstrates how the present results, which are obtained within the Born-Oppenheimer approximation (i.e. assuming an infinite mass of the impurity), deviate from the physically more correct values calculated using the reduced mass of the dimer system. While this deviation reaches as much as 20% for neon, it is only 6 % for argon, and further drops to only 3, 2 and 1 % for krypton, xenon, and SF_6, respectively. We conclude that for impurities with mass at least ten times larger than that of the ^{3}He atom, the Born-Oppenheimer separation is justified. Moreover, as shown in the last column in Table I, the energy is almost completely rectified by a simple diagonal non-adiabatic correction[27]:

$$E_{NA} = E_{He}^{kin} \times (m/M), \tag{1}$$

where E_{He}^{kin} is the kinetic energy of helium, and m and M are the masses of helium and the impurity, respectively.

Fig. 1 compares the radial ^{3}He wavefunctions for the five systems under investigation with numerically exact results employing either the full ^{3}He mass or the reduced mass of the complex. We see again that the finite Gaussian basis set is capable of providing accurate wavefunctions. Moreover, the accuracy of Born-Oppenheimer approximation improves with increasing mass of the impurity.

The next larger cluster is the Imp-(^{3}He)$_2$ complex, where already both the He-He interaction and the fermionic statistics start to play a role. Here, we present calculations for the SF_6 impurity which is most relevant from the experimental point of view. For the sake of simplicity, we have employed an isotropic, spherically averaged SF_6-He interaction potential.[25]

A complex with two ^{3}He atoms can be in a singlet or in a triplet state. In the former case, the proper quantum statistics is being taken care of via antisymmetrization of the spin part of the nuclear wavefunction. Therefore, the spatial orbital part, which is symmetric, is not influenced by the fermionic vs. bosonic nature of helium isotopes. The triplet state is, however, more interesting, since it can only be formed by fermionic ^{3}He atoms. In this case, the spin part of the wavefunction is symmetric and, therefore, it is the orbital part which has to be antisymmetrized. In the following, we discuss in detail the triplet state of the $SF_6(^3He)_2$ cluster.

Table II shows the total energies of the 1s and 1p states of the SF_6-^{3}He dimer, and of the triplet 1s1p state of the $SF_6(^3He)_2$ calculated by the Hartree-Fock method employing basis sets of increasing size. $\Delta E = E^{HF}_{1s1p} - E_{1s}$ is the stabilization energy of the dimer with respect to the SF_6-^{3}He and ^{3}He fragments. Since the hard-core He-He repulsion leads to a more diffuse wavefunction of the trimer compared with the dimer, it is necessary to employ a more diffuse basis set. Moreover, the p-functions are more diffuse than s-functions since they describe rotationally excited states of the dimer. Being more diffuse, i.e., more delocalized, the p-functions exhibit faster convergence with the basis set size. We have found that the following set of parameters provides a balanced description of both one-particle and two-particle wawefunctions: α_1^s=1.4, α_1^p=1.2, and g_s=g_p=1.45.

As shown in Table II, the convergence with basis set size is fast. Even though the converged values of the *absolute* energies of the one-particle orbitals (i.e., states of the SF_6-^{3}He dimer) are still 10 μhartree higher than the exact energies (see Table I), the error in the stabilization energy is much smaller due to cancelation of errors. For example, moving from the 13s11p to the 15s13p basis, the 3 μhartree change in one-particle energy is largely compensated by a similar decrease of Hartree-Fock energy of 4 μhartree, resulting in an overall change of only 1.2 μhartree in stabilization energy. Therefore, we can estimate the stabilization energy of a triplet to be equal to 22 μhartree.

The inclusion of He-He correlation will further stabilize the dimer. However, in the case of two ^{3}He atoms with the same spin, the correlation effects turn out to be very small, i.e., about 1 μhartree. This is clearly due to the Pauli exclusion principle (which is correctly described at the Hartree-Fock level) keeping the two fermions of the same spin apart from each other. Therefore, the effect of correlation is much smaller for the triplet state than for the corresponding singlet state (see Ref. 37 for analogous electronic structure examples). For the singlet state, however, as well as for larger clusters, correlation will certainly play a more prominent role. However, a promising strategy emerges from the present calculations: similarly to electronic structure problems, high-spin states are less correlated, and therefore they may serve as a good starting point for including correlation via the spin-flip method.[37]

It is interesting to compare the Hartree-Fock energy of -99 μhartree of the triplet state of the cluster to an estimate derived from the model of non-interacting helium atoms. Within the latter assumption, the energy of the $SF_6(^3He)_2$ cluster is simply the sum of energies corresponding to SF_6-^{3}He(1s) and SF_6-^{3}He(2p) complexes, which are, for the 15s13p basis, equal to -77 and -74 μhartree, respectively (see Table II). This leads to an estimate of the energy of the complex of -151 μhartree, which is 52 μhartree below the energy calculated from the two-particle wave wavefunction. The energy penalty of 52 μhartree is due to the hard-core He-He repulsion and quantum wavefunction delocalization.

Fig. 2 depicts the Hartree-Fock density of the triplet state of the $SF_6(^3He)_2$ cluster. Out of the three degenerate states, the one corresponding to the 1s1p_y configuration is shown. The density reflects the 1s1p structure of the triplet state, i.e., the superposition of s- and p-type orbitals. Note the delocalized character of the helium wavefunction around the central SF_6 dopant, and the corresponding excluded volume.

The present calculations represent the first applications of a novel methodology for the calculation of nuclear wavefunctions of doped ^{3}He clusters. In future work, the following lines of research will be pursued. The size of the systems will be increased up to several tens of helium atoms, in order to complete the first solvation shell around the dopant moiety, which plays a dominant role in solute-solvent interactions. Drawing from the analogy with electronic structure calculations, this is quite realistic. In particular, we expect that the number of necessary basis functions should scale mildly with the number of helium atoms, due to the very diffuse character of the nuclear wavefunctions. In larger clusters, correlation effects are expected to play a more prominent role. The recently proposed EOM-SF method, which uses a less correlated high-spin reference and treats final (low-spin) states as spin-flipping excitations,[37] is expected to be an appropriate strategy here. We also plan to implement non-isotropic helium-impurity interaction potentials which are more appropriate for molecular impurities. Since in the present model the impurity affects directly only the external potential, this is a relatively easy modification. Future work will also focus on the interpretation of the rotational spectrum of the dopant molecule in terms of excited nuclear states of the surrounding ^{3}He atoms. Finally, we note that the present methodology can also be directly applied to other fermionic quantum solvents, such as HD molecules. Possibly, it can also be extended to bosonic quantum systems like ^{4}He and molecular hydrogen nanodroplets.

IV. CONCLUSIONS

This paper presents the first calculations of nuclear wavefunctions and energies of doped ^{3}He clusters using a new approach based on a systematic quantum chemistry methodology. In this approach, the analogy between the doped ^{3}He cluster and an atomic system is exploited: fermionic helium atoms are treated as electrons, and the dopant acts as a source of external potential, similarly to nuclei in atoms.

We have adopted the well developed machinary of quantum chemistry for solving exactly or approximately the corresponding Schrödinger equation. A many-particle fermionic wavefunction is represented via an expansion over a many-particle basis set constructed from Slater determinants. Spin-orbitals are expanded over a finite set of Gaussian basis functions centered at the impurity. By using different strategies of generating many-particle basis set a series of systematic approximations to the exact wavefunctions is introduced.

A major difference between atomic electronic structure calculations and those for the doped ^{3}He clusters is in the different nature of the one- and two-body interactions — helium-dopant and helium-helium, respectively. Thus, the one-particle basis set construction and the integral evaluation algorithm are very different from those employed in electronic structure calculations. The equations for many-body wavefunctions, however, are identical for fermionic helium clusters and for electrons in molecular systems, which enables us to build upon the electronic structure formalism and computer codes.

Benchmark calculations are performed for a series of Imp-^{3}He (Imp = Ne, Ar, Kr, Xe, and SF_6) clusters. Results for the triplet state of the $SF_6(^3He)_2$ cluster, where the fermionic nature of the quantum solvent already has to be taken into account, are presented. Future applications to larger systems and anisotropic molecular impurities are discussed.

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FIGURE CAPTIONS

Figure 1:

Nuclear wavefunctions for a) Ne-^{3}He, b) Ar-^{3}He, c) Kr-^{3}He, d) Xe-^{3}He, and e)SF_6-^{3}He clusters. Comparison of the results obtained using a finite basis set of 15 Gaussians against numerically exact one-dimensional vibrational calculations (employing either the full ^{3}He mass or the reduced mass of the system) is shown. A multiplicative factor of $4\pi r^2$ is used for the former wavefunctions in order to unify normalization.

Figure 2:

^{3}He density for the triplet $1s1p_y$ state of $SF_6(^3He)_2$ shown in the XY plane (Z=0). The SF_6 molecule is at the origin of the coordinate frame. Note that the overall density is a superposition of s- and p- components.

TABLES

TABLE I. Total energies (μhartree) of Imp-^{3}He (Imp = Ne, Ar, Kr, Xe, and SF_6) complexes. Finite basis set calculations (15 Gaussians) versus numerically exact values employing the full ^{3}He mass or the reduced mass of the system. The last column shows the exact energies calculated with full ^{3}He mass, corrected for the diagonal non-adiabatic term.[18]

System	E^a_{15s}	E^a_{exact}	E^b_{exact}	$E^{b,c}_{exact}$
Ne-^{3}He	-10.19	-10.20	-8.05	-7.90
Ar-^{3}He	-27.28	-27.32	-25.74	-25.69
Kr-^{3}He	-29.30	-29.59	-28.82	-28.80
Xe-^{3}He	-29.32	-29.41	-28.95	-28.94
SF_6-^{3}He	-82.40	-86.59	-85.82	-86.59

[a] Full mass.

[b] Reduced mass.

[c] Full ^3He mass calculations corrected for the diagonal non-adiabatic term [see Eq. (1)].

TABLE II. Total energies (μhartree) of the 1s and 1p states of the SF_6-^{3}He dimer, and of the triplet 1s1p state of $SF_6(^3He)_2$ calculated by self-consistent field. ΔE is the stabilization energy of the dimer with respect to SF_6-^{3}He + ^{3}He.

Basis set[a]	$E_{1s}(SF_6\text{-}^3He)$	$E_{1p}(SF_6\text{-}^3He)$	E^{HF}_{1s1p} $(SF_6\text{-}(^3He)_2)$	Δ E
12s10p	-70.2	-69.5	-82.4	12.2
13s10p	-73.8	-69.5	-91.6	17.9
14s10p	-75.7	-69.5	-94.6	18.9
15s10p	-76.7	-69.5	-96.2	19.5
13s11p	-73.8	-72.6	-95.2	21.4
14s11p	-75.8	-72.6	-97.1	21.4
15s11p	-76.7	-72.6	-98.2	21.5
13s12p	-73.8	-73.4	-96.0	22.2
14s12p	-75.8	-73.4	-97.5	21.7
15s12p	-76.7	-73.4	-98.4	21.7
15s13p	-76.7	-73.5	-99.3	22.6

[a] α_1^s=1.4, α_1^p=1.2, g_s=g_p=1.45, 12 frozen virtual orbitals.

(a)

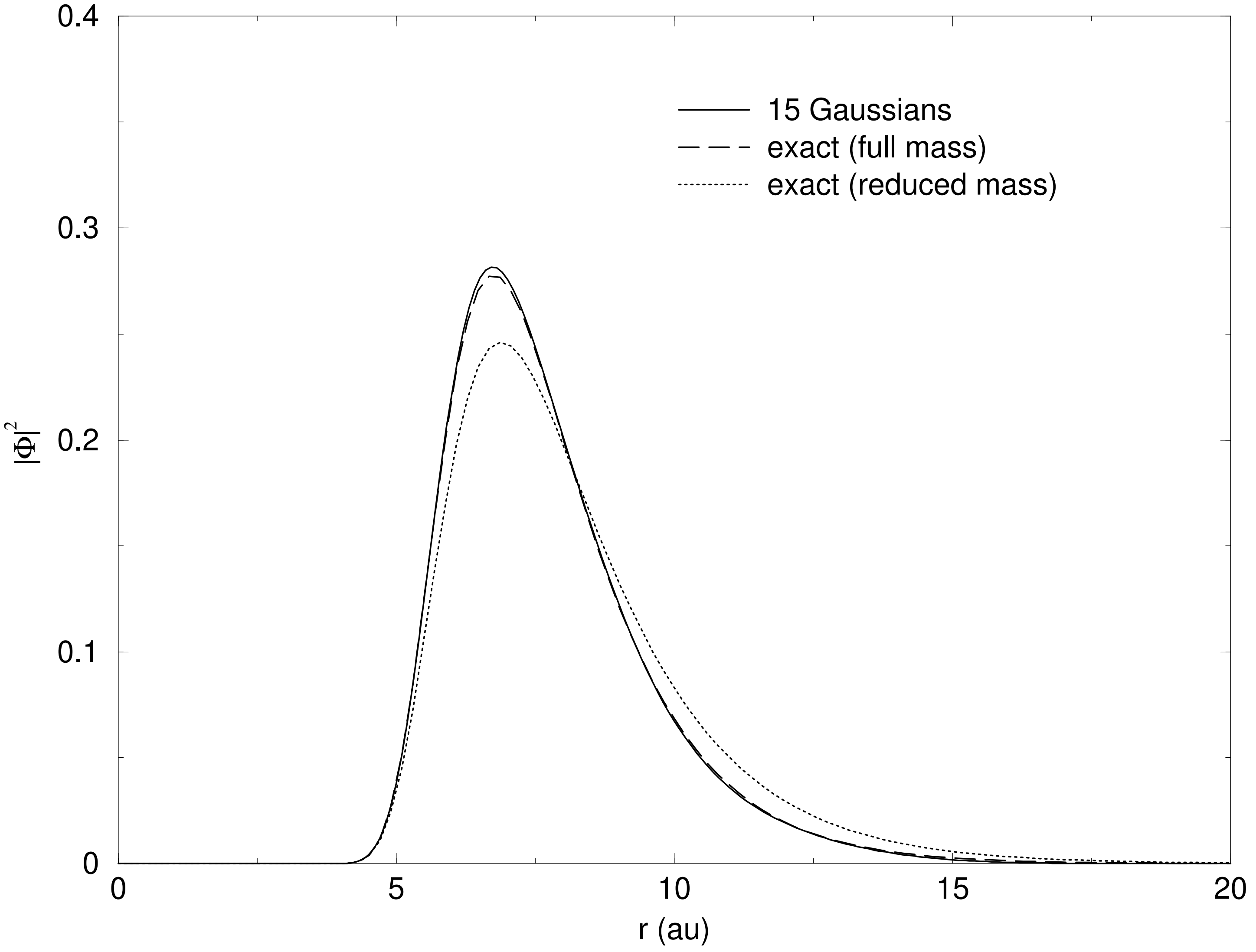

Figure 1a, Jungwirth and Krylov

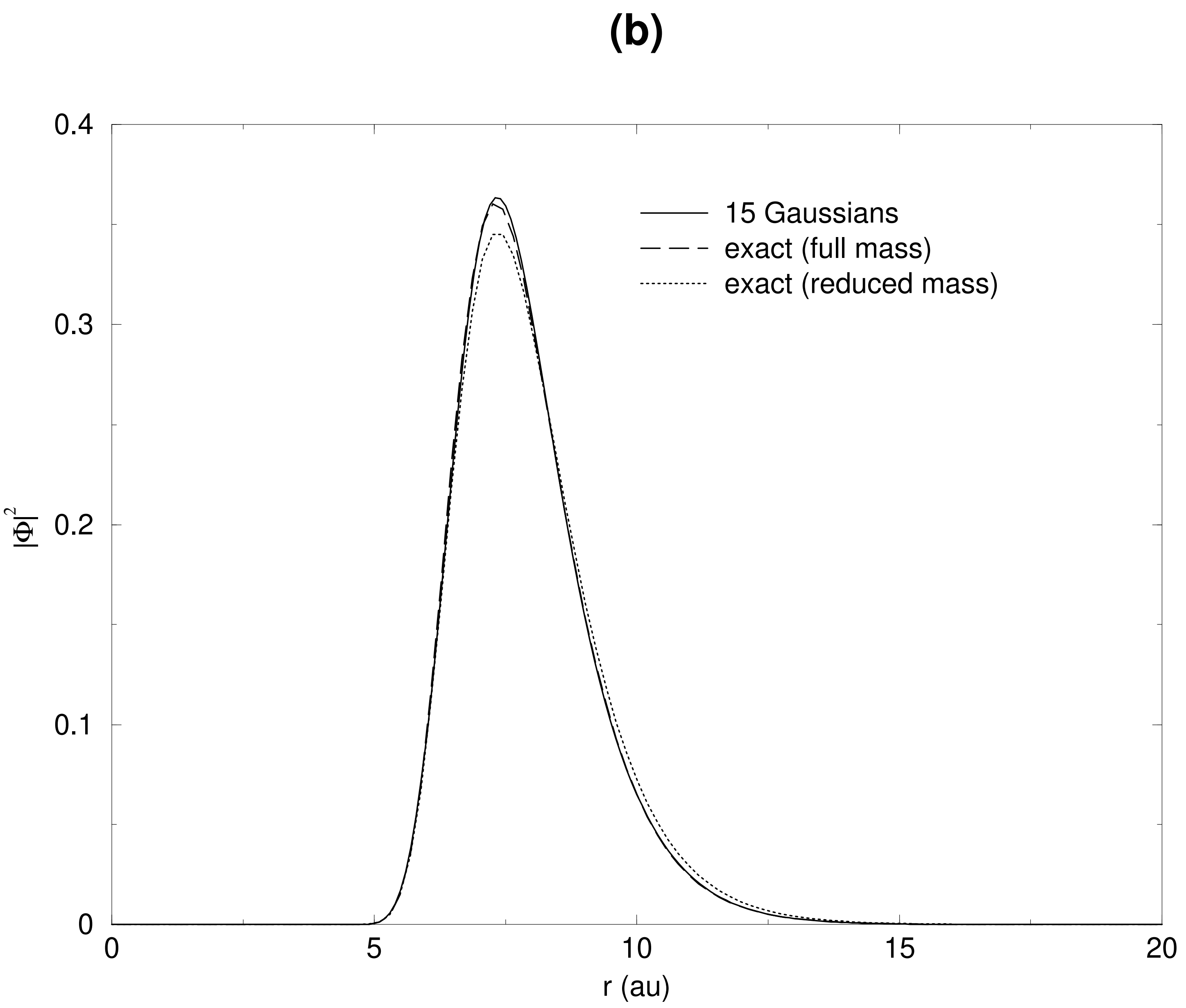

Figure 1b, Jungwirth and Krylov

(c)

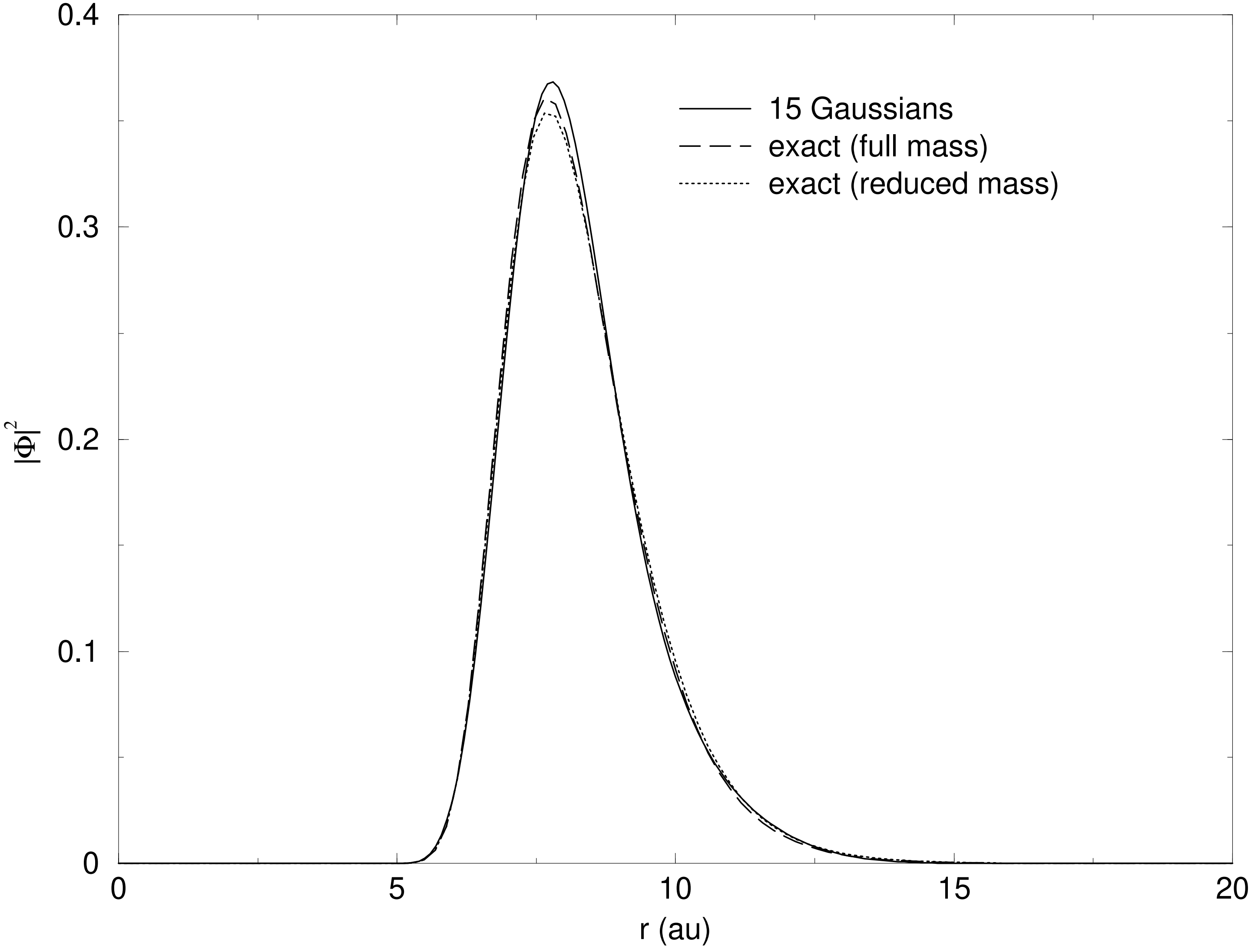

Figure 1c, Jungwirth and Krylov

(d)

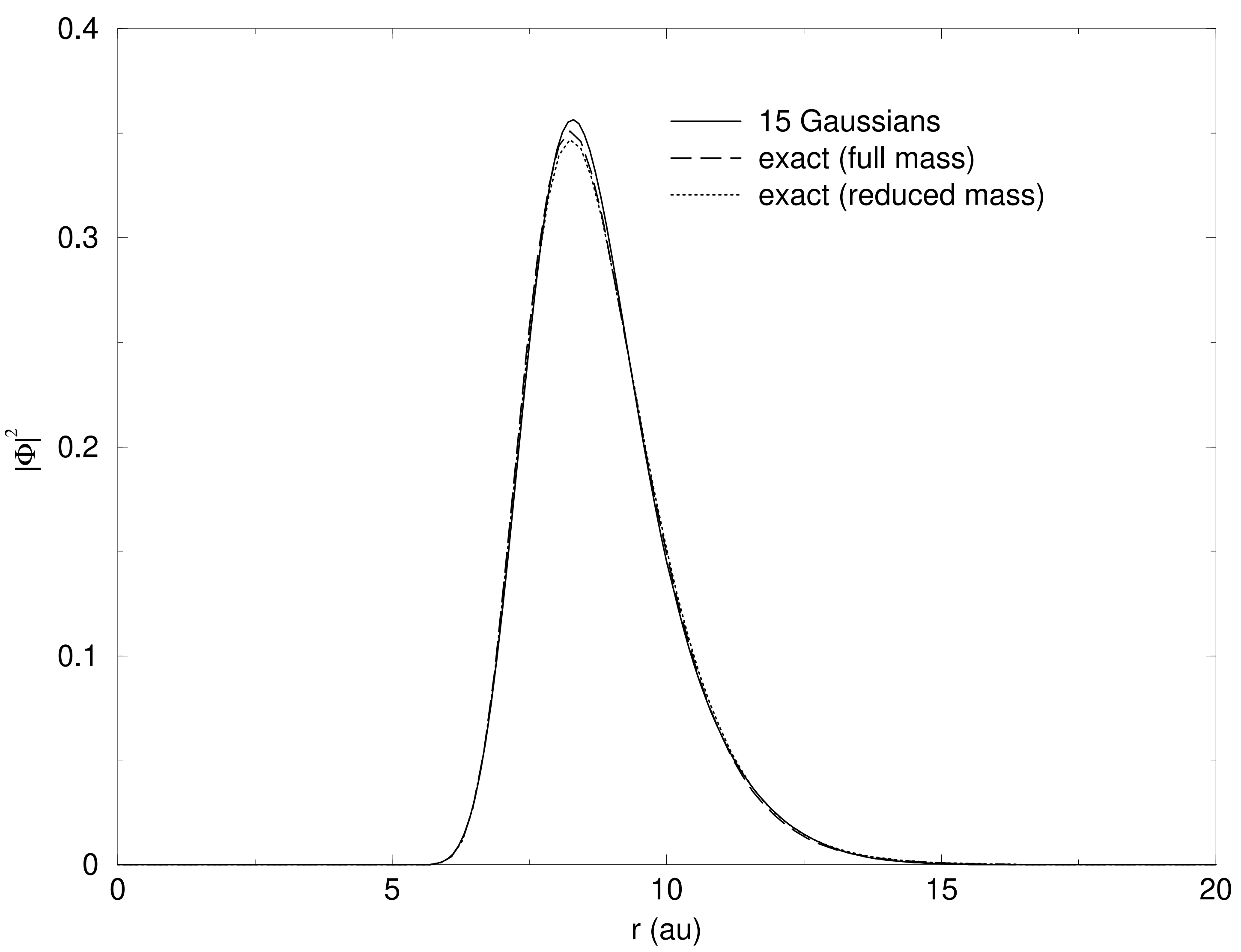

Figure 1d, Jungwirth and Krylov

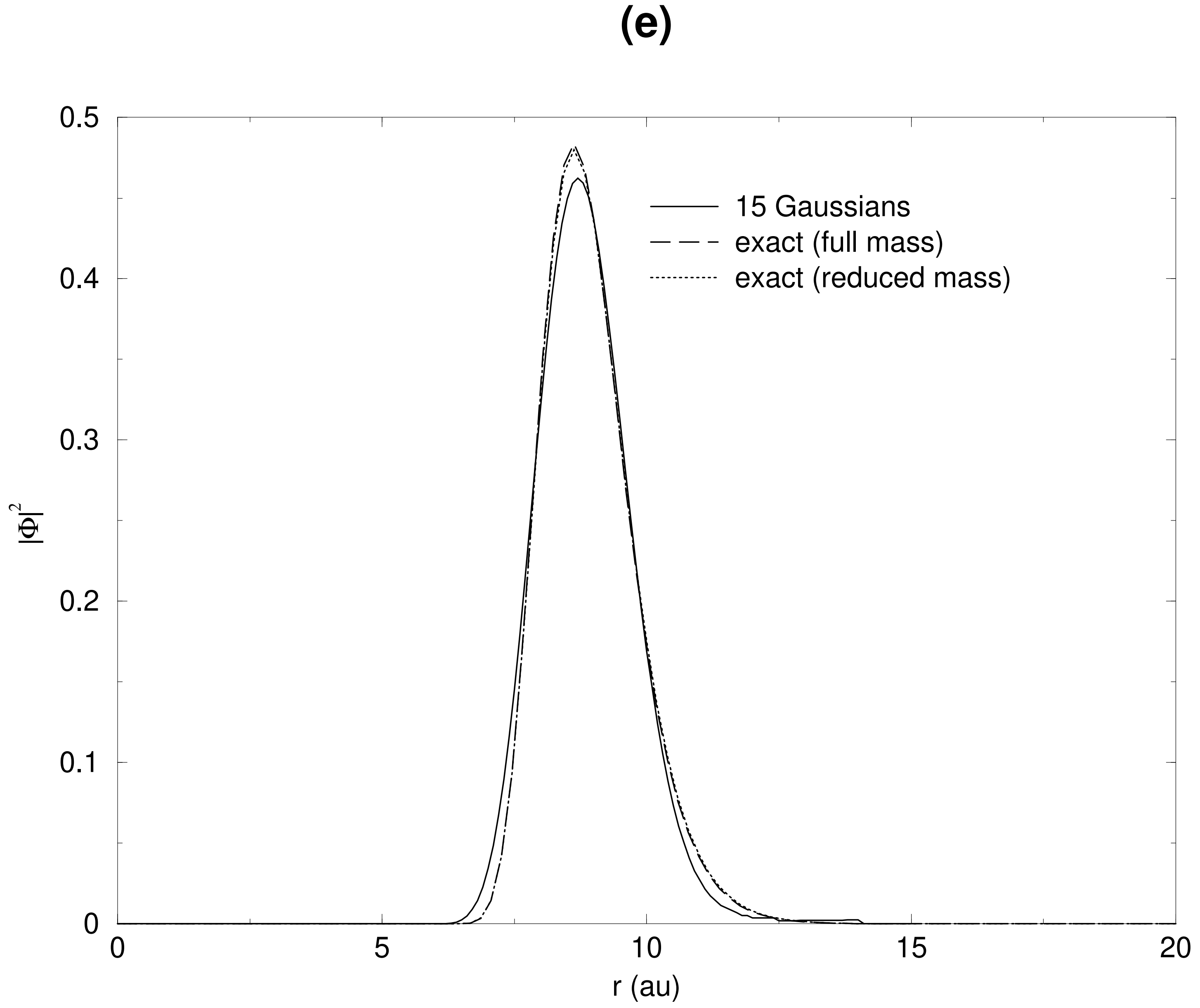

Figure 1e, Jungwirth and Krylov

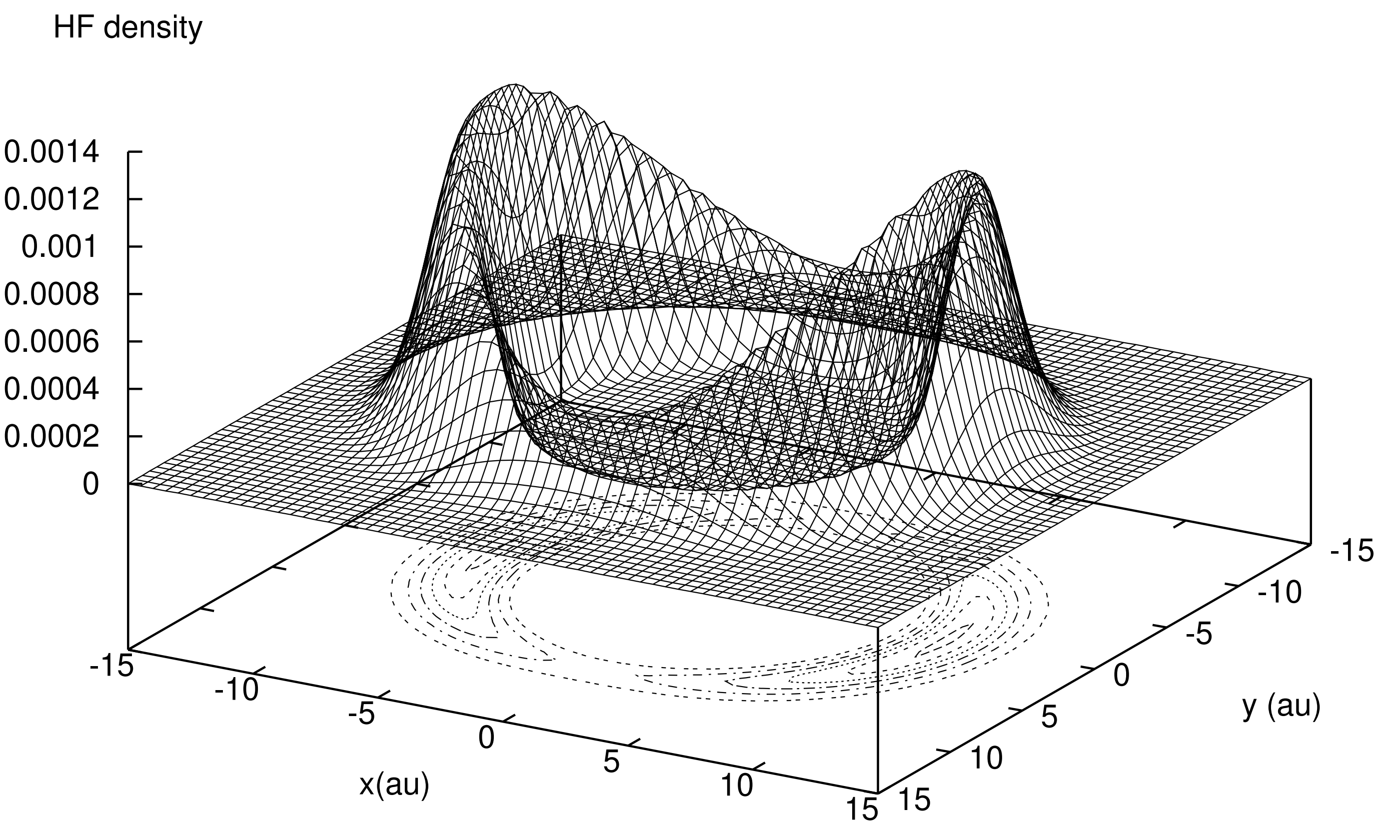

Figure 2, Jungwirth and Krylov