Extension of the wave packet molecular dynamics method towards the accurate quantum simulations of electron dynamics

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Abstract. In this paper, we review a multiple-wavepacket version of the Antisymmetrized Wave Packet Molecular Dynamics (AWPMD), that may be utilized to increase the accuracy and the performance of this quantum simulation method. The original WPMD method is based on parameterization of the electron wave function by a single Gaussian wave packet. It gives qualitatively better results than the classical Molecular Dynamics but the quantitative description of essentially quantum systems is rather poor. In this work, we describe a new technique based on multiple Gaussian expansion of the single-electron wave function, which is called Split Wave Packet Molecular Dynamics (SWPMD). The related theoretical formalism is given, followed by the analysis of static and dynamical properties of a quantum system of several particles, where the simulation results may be compared to the theoretical predictions. The tests are based on ionization of hydrogen atom under a strong laser pulse. We demonstrate that the SWPMD method may significantly improve the accuracy of the model wave function and enables one to simulate the quantum branching processes, including the tunneling, which was impossible in the single-wavepacket version of the method.

1. Introduction
Microscopic numerical models of nonideal (strongly coupled) plasmas, especially describing the non-equilibrium state, are important for understanding the plasma formation processes where high energy deposition rates are expected, for example, laser ablation [1, 2]. The methods of classical Molecular Dynamics (MD) and Monte Carlo (MC) are successfully applied to study nonideal plasmas at moderate electron number densities (about $10^{21} \text{ cm}^{-3}$ for hydrogen plasma) and relatively high temperatures (over $10^4 \text{ K}$) [3–6]. At lower temperatures and/or higher densities, the use of the electron-ion and electron-electron pseudopotentials introduces considerable ambiguity in the plasma thermodynamics and relaxation rates. The use of electron-ion pseudopotentials in classical molecular dynamics simulations of nonideal plasmas restricts the applicability of this method to high temperatures, high ionization degrees and near equilibrium states.

Quantum methods such as DFT, applied to plasma simulations, are much more computationally demanding than the classical MD. Moreover, these methods are mostly not capable to handle the dynamics of electrons. There are several techniques to overcome these limitations. One of them is Wave Packet Molecular Dynamics (WPMD), where electron quantum
dynamics is approximated by propagation of wave packets, parameterized by a small number of dynamic variables [7–10]. The exchange interaction between electrons of the same spin in the Hartree–Fock limit can be taken into account using antisymmetrized wave packets [10]. WPMD has another advantage of being rather computationally efficient, especially in the non-antisymmetrized (Hartree) version. The formal scaling of computational effort with the number of particles $N$ for this method ranges from $N \log(N)$ (Hartree) to $N^4$ (AWPMD). As seen in the following, the main computational effort of AWPMD is concentrated on the Coulomb matrix elements calculation, so the method performance is expected to be compute-bound rather than limited by the computer memory or network bandwidths. This makes hardware-orientated optimization of AWPMD for many-core computer architectures quite promising [11].

The area of very high plasma densities (about $10^{23}$ cm$^{-3}$ for hydrogen plasma) and low temperatures (less than $10^4$ K) is well described by the WPMD/WPMC methods [9] including the version with antisymmetrized wave functions for electrons with the same spin (AWPMD) [10]. These methods, however, are not directly applicable to higher temperatures due to the model breakdown caused by spreading of the wave packets for weakly bound electrons [12, 13].

Poor accuracy for electronic bound states at ions and spreading of wave packets for weakly bound electrons are known problems of the existing WPMD models for nonideal plasmas. In our earlier work [14] we proposed to address both issues using a new technique based on multiple Gaussian expansion of the single-electron wave function, which is called Split Wave Packet Molecular Dynamics (SWPMD). The main features of SWPMD are the better representation of bound electron and the ability to study electron dynamics taking into account the wave function branching [15]. In this work, we evaluate this new approach in greater detail using a dynamic test such as calculation of ionization of an atom in a strong laser field.

In Section 2 the main definitions used in SWPMD method are outlined including additional general formulae of the Hamiltonian for both antisymmetrized and non-antisymmetrized cases. The correct description of the ionization and recombination processes is crucial for the model. To check the accuracy of different methods as applied to ionization we modified the code and performed test simulations of a single bound electron (hydrogen-like atom) in an external electric field using both the Classical Trajectories Monte-Carlo (CTMC) and Split WP techniques. Section 3 presents the benchmarks of the method using static and dynamic test problems. Additional analysis of the system state based on the wave function spectrum is given in Section 4.

2. Split WP technique

2.1. Basic formulae

The traditional WPMD algorithm [7–10] implies the use of a single Gaussian to represent each electron in the model. This representation has two deficiencies: poor accuracy of atomic/molecular bound states and inability to describe quantum branching. The second problem is very important for correct quantum picture of ionization and recombination. In the true quantum dynamics, some part of a single electron density may remain bound after a collision, whereas the other part contributes to the ionized or scattered electron motion. This process cannot be described by a single Gaussian.

The WPMD technique allows the description of such processes when single electron wave functions are represented by multiple Gaussians, each having its own set of parameters, which we refer to as a Split WP method. It may be implemented in a straightforward way without changing the global scaling of the algorithms with the number of particles. The basic formulae for this method are given below and test cases are considered in the next section. In the following we use Latin letters for electron indices. For individual wavepackets the indices are either Greek letters or pairs of Latin and Greek letters, like $\alpha$, where we emphasize that the wavepacket belongs to a certain electron.

In the Split WP formulation the trial wave function $\phi_k$ of an $k$-th electron is given as a
normalized sum of multiple Gaussian wavepackets $\varphi_{k\alpha}$:

$$\phi_k(x) = n_k^{-1/2} \sum_{\alpha=1}^{M_k} c_{k\alpha} \varphi_{k\alpha}(x),$$ (1)

$$\varphi_{k\alpha}(x) = \left( \frac{3}{2\pi \sigma_{k\alpha}^2} \right)^{3/4} \exp \left\{ -\left( \frac{3}{4\sigma_{k\alpha}^2} \frac{i p_{s,k\alpha}}{2n_{s,k\alpha}} \right) (x - r_{k\alpha})^2 + i \frac{\mathbf{p}_{k\alpha} \cdot (x - r_{k\alpha})}{\hbar} \right\}.$$ (2)

Each wave packet has a traditional set of dynamic variables $\mathbf{q} = \{\mathbf{x}, \mathbf{p}, \gamma, p_{\gamma}\}$ [7] and an additional complex variable $c$. The number of wavepackets may be different for different electrons. The norms $n_k$ are given by $n_k = \sum_{\alpha, \beta} c_{k\alpha}^{*} c_{k\beta} a_{k\alpha} b_{k\beta}$, where $a_{k\alpha} = \langle \varphi_{k\alpha} | \varphi_{j\beta} \rangle$ is the overlap between the contributing wavepackets of electrons $i$ and $j$.

Let us assume that the Hamiltonian of the many-electron system interacting with ions reads

$$\hat{H} = \hat{T}_e + \hat{T}_{ei} + \hat{V}_{ei} = \sum_k N_e \sum_{l,m} \frac{\mathbf{p}_k^2}{2m} - e^2 \sum_{k,j} N_j \frac{Z_j}{|\mathbf{r}_k - \mathbf{r}_j|} + e^2 \sum_{k,l} N_e \frac{1}{|\mathbf{r}_k - \mathbf{r}_l|}.$$ (3)

Then the matrix elements are easily calculated using the formulae for the elementary Gaussian matrix elements for single-electron energies (kinetic energy of electrons and electron-ion interaction)

$$t_{kl}^e + t_{kl}^{ei} = \langle \varphi_k | \hat{T}_e + \hat{T}_{ei} | \varphi_l \rangle = n_k^{-1/2} n_l^{-1/2} \sum_{\alpha, \beta} c_{k\alpha}^{*} c_{\beta}(t_{kal}^e + t_{kal}^{ei})$$ (4)

and two-particle energies (Coulomb repulsion of electrons)

$$v_{klmn} = \langle \varphi_k \varphi_l | \hat{V} | \varphi_m \varphi_n \rangle = (n_k n_l m_n n_m)^{-1/2} \sum_{\alpha, \beta, \gamma, \delta} c_{k\alpha}^{*} c_{\beta} c_{m\gamma} c_{\delta} v_{kal\beta m\gamma\delta}.$$ (5)

### 2.2. Calculation of the Hamiltonian derivatives

For the calculation of the forces, derivatives of the energies with respect to all WP variables, including $c$ coefficients should be calculated. It is convenient to represent each elementary (calculated over simple Gaussians) matrix element as a product of overlaps and some residual $R$: 

$$t_{kl}^{ei} = o_{\alpha\beta} R_{\alpha\beta}^{ei} \quad R_{\alpha\beta}^{ei} = -\frac{h^2}{2m} \left[ \frac{(b_{\beta} a_{\alpha}^* - b_{\alpha} a_{\beta}^*)^2}{a_{\alpha\beta}^2} - 6 \frac{a_{\alpha}^* a_{\beta}}{a_{\alpha\beta}} \right],$$ (6)

$$v_{klmn} = o_{\alpha\beta} v_{\alpha\beta} R_{\alpha\beta}^{ei} \quad R_{\alpha\beta}^{ei} = \sum_i \frac{q_i}{g_{\alpha\beta i}} \text{erf} \{ g_{\alpha\beta i} \sqrt{a_{\alpha\beta}} \},$$ (7)

$$v_{\alpha\beta\gamma\delta} = o_{\alpha\gamma} v_{\alpha\beta\gamma\delta} R_{\alpha\beta\gamma\delta}^{ee} \quad R_{\alpha\beta\gamma\delta}^{ee} = \frac{1}{|\Delta_{\alpha\gamma} - \Delta_{\beta\delta}|} \text{erf} \left\{ \frac{|\Delta_{\alpha\gamma} - \Delta_{\beta\delta}|}{\sqrt{a_{\alpha\beta}^2 + a_{\alpha\gamma}^2}} \right\},$$ (8)

where

$$\Delta_{\alpha\beta} = \frac{b_{\alpha\beta}}{2 a_{\alpha\beta}}, \quad g_{\alpha\beta i} = \Delta_{\alpha\beta} - r_i, \quad g_{\alpha\beta i} = |g_{\alpha\beta i}|.$$ (9)

Then the derivatives of the overlap elements and the residuals with respect to WP parameters should be calculated. Let us introduce a new variable:

$$d_{kq} = n_k^{-1/2} \left( \mathbf{n}_k \right)^q = -\frac{(n_k)^q}{2n_k},$$ (10)
which is the derivative of a single electron norm with respect to some parameter $q$. If $q$ is a wave packet parameter $\gamma$, then the expression for $d$ reads:

$$d_{wq\gamma} = -n_w^{-1} \Re c_{w\gamma} \sum_\beta e_{w\beta}(o_{w\beta w\gamma})'_{q\gamma}.$$  (11)

For $q$ being a complex coefficient $c_{w\gamma} = \Re c_{w\gamma}, \Im c_{w\gamma}$ before wave packet $\gamma$ of the wave function of electron $w$, the expressions for $d$ read:

$$d_w \Re c_{w\gamma} = -n_w^{-1} \Re \sum_\beta c_{w\beta}^* o_{w\beta w\gamma},$$  (12)

$$d_w \Im c_{w\gamma} = n_w^{-1} \Im \sum_\beta c_{w\beta}^* o_{w\beta w\gamma}$$  (13)

for real and imaginary components of $c$ correspondingly.

Finally the following expressions for the derivatives of the two-electron matrix elements $t^{e}_{\alpha\beta}$ or $t^{e}_{\alpha\gamma}$ with respect to the parameters entering the left ("bra-") side of the matrix element can be obtained:

$$\left( t^{e}_{w\alpha} \right)'_{q_{w\gamma}} = 2(n_w n_1)^{-1/2} \Re \left( c_{w\mu}^* \sum_\beta c_{\beta\gamma}^* \left[ \left( R^{e}_{w\gamma\beta} \right)'_{q_{w\gamma}} o_{w\gamma l \beta} + R^{ee}_{w\gamma\beta} (o_{w\gamma l \beta})'_{q_{w\gamma}} \right] \right),$$  (14)

$$\left( t^{e}_{w\alpha} \right)_{\Re c_{w\gamma}} = 2(n_w n_1)^{-1/2} \Re \sum_\beta c_{\beta\gamma} t^{e}_{w\gamma l \beta} + t^{e}_{w l} d_w \Re c_{w\gamma},$$  (15)

$$\left( t^{e}_{w\alpha} \right)_{\Im c_{w\gamma}} = 2(n_w n_1)^{-1/2} \Im \sum_\beta c_{\beta\gamma} t^{e}_{w\gamma l \beta} + t^{e}_{w l} d_w \Im c_{w\gamma}.$$  (16)

The derivatives for the "ket-" sides have the similar form with indices permutation.

The derivatives of the four-electron matrix elements $v_{\alpha\beta\gamma\delta}$ with respect to the parameters entering the left ("bra-") side of the matrix element read

$$\left( v^{ee}_{wlmn} \right)'_{q_{w\mu}} = 2(n_w n_1 n_m n_n)^{-1/2} \Re \left( c_{w\mu}^* \sum_{\beta,\gamma,\delta} c_{\beta\gamma}^* c_{\gamma\delta}^* o_{\gamma\delta \beta} \left[ \left( R^{ee}_{w\delta\gamma} \right)'_{q_{w\gamma}} o_{w\delta l \beta} \right] \right),$$  (17)

$$\left( v^{ee}_{wlmn} \right)_{\Re c_{w\mu}} = 2(n_w n_1 n_m n_n)^{-1/2} \Re \sum_{\beta,\gamma,\delta} c_{\beta\gamma} v^{ee}_{wld\gamma} + v^{ee}_{wl\mu} d_w \Re c_{w\mu},$$  (18)

$$\left( v^{ee}_{wlmn} \right)_{\Im c_{w\mu}} = 2(n_w n_1 n_m n_n)^{-1/2} \Im \sum_{\beta,\gamma,\delta} c_{\beta\gamma} v^{ee}_{wld\gamma} + v^{ee}_{wl\mu} d_w \Im c_{w\mu}.$$  (19)

For computational purposes it is convenient to calculate all derivative terms inside a single loop spanning wave packet indices and accumulate the contributions in the force vector without storing any temporary terms. For example, for the two-electron matrix elements energy derivatives are accumulated as sums of contributions like

$$\left[ t^{e}_{k\alpha} \right]'_{q_{k\alpha}} = (n_k n_1)^{-1/2} \left( c_{k\alpha}^* c_{\beta\gamma}^* t^{e}_{k\alpha} \right)'_{q_{k\alpha}} + c_{k\alpha}^* c_{\beta\gamma} t^{e}_{k\beta\gamma} d_{k\alpha},$$  (20)

where $q_{k\alpha}$ is one of the parameters (including $c$ coefficients). These derivative contributions are easily calculated together with energy terms $t^{e}_{k\beta\gamma}$ in the loop spanning all wave packet pairs. Analogously, contributions from the four-electron term derivatives are calculated together with the four-center integrals by the loop spanning all wave packet quadruples.
2.3. Quantum approximations for the trial wave function

The simplest approximation for the many electron trial wave function is the product of the corresponding single-electron wave functions (Hartree product):

\[ \Psi_h(\{x_k\}, t) = \prod_k \phi_k(x_k, t). \] (21)

For the Hartree case (no antisymmetrization) the total energy of a system of \( N \) electrons is given by

\[ E = \sum_k (t_{kk}^e + t_{kk}^o) + \sum_{k,l} v_{klkl} \]

\[ = \sum_k n_k^{-1} \sum_{\alpha,\beta} c_{\alpha k}^* c_{\beta k} t_{\alpha k \beta} + \sum_{k,l} n_k^{-1} \sum_{\alpha,\beta,\gamma,\delta} c_{\alpha k}^* c_{\beta l} c_{\gamma l} c_{\delta k} v_{\gamma k \alpha \beta \delta}. \] (22)

For multiple Gaussian wave packet representation, the norm matrix is not simplectic even for the Hartree approximation. In this case the norm has block-diagonal form with the diagonal blocks corresponding to each electron. The block sizes are determined by the number of the wavepackets contributing to an electron. The norm matrix block for \( i \)-th electron reads

\[ N_{q_i \alpha q_i \beta} = -2\hbar \text{Im} \left[ \langle \phi_i' | \phi_i' \rangle_{q_i \alpha} - \langle \phi_i' \rangle_{q_i \alpha} \langle \phi_i | \phi_i' \rangle_{q_i \beta} \right]. \] (23)

Let us introduce an auxiliary matrix

\[ L_{ijq_\alpha} = \langle \phi_i | \phi_j' \rangle_{q_\alpha} = (n_i n_j)^{-\frac{1}{2}} \sum_{\beta} \langle \phi_i | \phi_j' \rangle_{q_\alpha} = (n_i n_j)^{-\frac{1}{2}} \sum_{\beta} \langle \phi_i | \phi_j' \rangle_{q_\alpha} = \left[ (n_i n_j)^{-\frac{1}{2}} \right]_{\alpha=\beta, \alpha'=-\alpha}. \] (24)

In this formula the overlap derivative is always taken first with respect to the parameter at the right ("-ket") side of the overlap, and then the actual parameters are substituted, so the sum item is nonzero even for a single packet (when \( i = j, \alpha = \beta \)). \( L \) is a square matrix with the first dimension being the number of electrons and the second being the number of wave packet parameters in the system. For the Hartree case only the blocks with \( i = j \) are needed, so the matrix storage may be greatly reduced. Using \( L \) matrix, the norm matrix block for the Hartree case may be rewritten as

\[ N_{q_i \alpha q_i \beta} = -2\hbar \text{Im} \left[ n_i^{-1} \langle \phi_i | \phi_i' \rangle_{q_\alpha} + L_{i\alpha i\alpha} + \sum_{i,i' \alpha} d_{i\alpha \beta} d_{i'\alpha \beta} - L_{i\alpha i\alpha} L_{i\alpha i\alpha} \right]. \] (25)

The expressions for the antisymmetrized trial wave functions may be derived in the analogous way (see [14]).

For the Split WP method, the equations of motion are not simplectic even for the Hartree approximation

\[ \frac{d q_i}{dt} = \sum_j (N^{-1})_{ij} \partial H \partial q_j. \] (26)

In this case the norm matrix \( N \) has a block-diagonal form with the diagonal blocks corresponding to each electron. The block sizes are determined by the number of the WPs \( M_k \) contributing to an electron. As noted before all Hamiltonian derivatives and the norm matrix elements in (26) are derived analytically as functions of the dynamic variables.

One of the possible versions of the presented energy expansion is the unnormalized SWPMD method, were the norm prefactors \( n_k \) are not included in the equations (supposed to have a
In this case, the electron norm conservation should be maintained externally, for example as a set of additional conditions solved together with the time evolution equations. This unnormalized form has an advantage of resolving the proper wave function phase in course of the WP propagation. Here the variables \( c(t) \) act as quantum time-dependent basis expansion coefficients. The phase information is important for the spectral analysis of the wave function (see below). For a one-electron system, such as a hydrogen atom, the norm of the electron is an integral of motion and therefore no additional constraints should be imposed for the unnormalized SWPMD method. In this case both normalized and unnormalized versions result in the same variable trajectories within numerical error, so they may be used equivalently for dynamic properties calculation.

3. Dynamic properties: ionization of the hydrogen atom

Calculations of the ground state energies of H and He performed in [14] showed that the SWPMD method provides accuracy of less than 1% for even three WPs per electron. In the case of helium, the exchange interaction between electrons with the same spin can be taken into account using antisymmetrization of the total electron wave function which is in a good agreement with the unrestricted Hartree–Fock approach.

As a benchmark for dynamical properties the ionization of a hydrogen atom in a strong laser pulse was considered [14]. For comparison we referred to Classical Trajectory Monte-Carlo (CTMC) simulations and numerical integration of the time-dependent Shr"odinger equation. The results of SWPMD method were in a good agreement with the quantum mechanical calculations in the cases when the CTMC approach fails. In this paper we performed additional studies of the ionization problem.

Let us recall the simulation scheme used in [14]. Initially an atom is prepared in the ground state using energy minimization. In should be noted that in SWPMD the pure Coulomb electron-ion interaction potential is used opposed to the classical MD where in most cases pseudopotentials are applied [4,5,16]. Then the atom is affected by a linearly polarized laser pulse with the electric field defined by \( E_z(t) = E_0 \sin^2 [\pi t/(2T)] \cos(\omega_L t) \) where \( E_0 \) is the amplitude, \( 2T \) is the pulse duration, \( \omega_L \) is the laser frequency. For very short pulse durations, this can be considered as a reasonable approximation to describe collisional ionization in plasma caused by electric field of a projectile particle, not a real laser pulse.

The evolution of the main WP parameters is monitored for a certain time after the pulse. In an example presented in figure 1 due to a higher laser intensity only one WP remains bound at the end of the laser pulse. After the pulse it still oscillates around the ion which implies that it can be described by a composition of excited states. Analysis of such states will be given in the next section.

The wave packets are marked as bound if their energy is negative. Using this criterion, we can now split the total WP into the two parts:

\[
\psi = \psi_{\text{bound}} + \psi_{\text{free}},
\]

where

\[
\psi_{\text{free}} = \sum_{i: E_i \geq 0} c_i \phi_i, \quad \psi_{\text{bound}} = \sum_{i: E_i < 0} c_i \phi_i.
\]

Then the ionization probability can be defined as the ratio between the norm of the free WPs to the total norm

\[
w = \frac{\langle \psi_{\text{free}} | \psi_{\text{free}} \rangle}{\langle \psi | \psi \rangle}.
\]

The values of the ionization probability obtained in this way are shown in figure 2 by stars. It is seen that they are much closer to the quantum mechanical results (crosses) obtained in [17].
Figure 1. Evolution of the total wave function $|\phi(z)|^2$ depending on time. The total number of WP is $N_{wp} = 5$, the half pulse length is $T = 0.6\text{fs} = 25\text{a.u.}$, the pulse amplitude is $E_0 = 0.05\text{a.u.}$

At the same time, they are less precise than CTMC for long pulse durations due to numerical instability in WPMD caused by the norm matrix calculations.

In addition to that result we performed comparison with another conditions of the laser pulse used in [18] to evaluate their calculations of hydrogen ionization probability based on expansion into multiple ion-centered non-spherical Hermite–Gaussian functions (figure 3). It is seen that the present SWPMD simulations are in a good agreement with the most accurate QPROP model presented in the article. Results for five and six WPs converge with a small numerical error.

4. Wave function spectrum and excited states of an atom

Time evolution of the total wave function provided by the SWPMD method may be used to obtain energy spectrum of the system. To retain the proper phase of the total wave function we should refrain from the unnormalized version the algorithm, where the expansion coefficients of the multiple Gaussians for the electron are not constrained at each timestep. The evolution of the conservative quantum system may be represented as

$$|\psi(t)\rangle = \sum a_i e^{-i\frac{E_i}{\hbar}t} |\chi_i\rangle,$$

where $a_i$ are the expansion coefficients of the system initial state into the eigenstates basis with the wave functions $|\chi_i\rangle$ and the eigen energies $E_i$. Here we assume that the sum also represents the integral of the positive continuous part of the spectrum.

For the exact quantum solution the energy spectrum (all coefficients $a_i$ corresponding to different energies) may be obtained as the Fourier transform $\tilde{C}(E)$ of the following correlation function

$$C(t) = \langle \psi(0) | \psi(t) \rangle \sim \sum |a_i|^2 e^{-i\frac{E_i}{\hbar}t}.$$  

In the case of the approximate variational SWPMD solution, we may use the same correlation function to trace the existence of the correlation peaks at the energies corresponding to the eigenstates of the system.
We have applied the above technique to the problem of the hydrogen atom ionization described in the previous section. The initial state $|\psi(0)\rangle$ was selected after the end of the laser pulse, then $C(t)$ was obtained numerically from the overlaps of the time-dependent SWPMD solution and the recorded wave function $|\psi(0)\rangle$. The specific time position of the initial state did not influence the spectral result, which indicates that the spectrum is conserved for the variational solution as well. Because of the time symmetry of the quantum correlation function ($C(-t) = C^*(t)$) we also assumed this symmetry for the numerically measured $C(t)$, symmetrically expanding it to the negative time range. Then the complex FFT analysis was performed, resulting in a spectrum shown as example in figure 4a. Because of the approximate nature of the variational solution, the spectrum contains both positive and negative components. However, the integration of this spectrum with the energy reveals that the integral is always positive for any energy window that is large enough compared to the high-frequency spectral oscillations.

Analysis of the integrated energy spectra may serve as an independent ionization criterion for the problem of laser ionization of an atom. The ionization probability is obtained then as a fraction of the spectrum in the positive (continuous) energy range:

$$w_{\text{spec}} = \frac{\int_{0}^{+\infty} \tilde{C}(E)dE}{\int_{-\infty}^{+\infty} \tilde{C}(E)dE}.$$

(32)

This criterion agrees well with the WP-based one, which was described in the previous section. The comparison between ionization probabilities obtained by different methods is presented in
Figure 4. (a) Sample spectrum of the correlation function \( I(E) \). Dashed lines show the position of the ground \( E_0 \) and first excited \( E_1 \) states of the atom. (b) Ionization probability for energy and spectral ionization criteria depending on the number of WPs.

It is seen that the spectral criteria provides non-zero results for small WP number and better convergence for large WP number although it requires longer simulation time to reduce numerical errors.

Moreover, the spectral analysis may be used for tracing excited states of a system in the time dependent wave function. To do that a linear response technique (similar to that used in the time-dependent DFT method) may be applied. The system is subjected to a small amplitude excitation of a given frequency and the resonances indicate the transitions to the excited states. The dependence of the photon absorption energy on the signal frequency for the hydrogen atom is shown in figure 5. The clearly seen resonance is shifted by \( \sim 0.01 \) a.u. from the exact value. Being excited this transition results in the peak at the 2s energy level shown in figure 4a.

5. Conclusions
In this work, we summarized our results on the implementation and testing of a new multiple-Gaussians WPMD method. The probability of ionization of the hydrogen atom predicted by the new method was compared with the results of other authors for two sets of laser pulse parameters. It is shown that the total wave function spectrum can be used to obtain an alternative ionization criterion and to observe excited states of an atom. As was shown, the accuracy of a wave function representation and the corresponding accuracy of energies and phase space occupation probabilities increases with the proposed extension of the method. We note that the splitting technique was so far tested on small systems and on quantum events, which have well-defined initial or final states. For a system of many particles, for example, for the model of electron-ion plasma, allowing frequent branching of every wavepacket would result in exponential growth of the number of wavepackets and thus would become impractical. Therefore, a suitable wave packet collapse/reordering procedure, similar to the microscopic event-based dynamics proposed in [19] is needed to maintain the limited number of wave packets in the system. Another use of the spitting technique within the plasma model would be keeping a certain number of wave packets with vanishing amplitudes attached to positive ions. These “recombination sites” will provide a basis for possible recombination events, which is largely suppressed in the standard
Figure 5. Dependence of the absorbed energy on the laser frequency for a small amplitude laser pulse in the area of 1s \( \rightarrow \) 2s transition; \( N_{wp} = 5 \), \( T = 200 \) a.u., \( E_0 = 0.005 \) a.u.

WPMD method because of the single-centered shape of the electron wave function.

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