Two methods for restricted configuration spaces within the multiconfiguration time-dependent Hartree-Fock method

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Two methods for restricted configuration spaces within the multiconfiguration time-dependent Hartree-Fock method

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The MCTDHF method has shown promise in calculating electronic dynamics in molecules driven by strong and high energy lasers. It must incorporate restricted configuration spaces (meaning that a particular combination of Slater determinants is used, instead of full configuration interaction) to be applied to big systems. Two different ansatzes are used to determine the essential term in the equations. The first ansatz is the Lagrangian variational principle. The explicit, complete MCTDHF equations of motion, satisfying that principle, for arbitrary configuration spaces, are given. The property that a restricted configuration list must satisfy in order for the Lagrangian and McLachlan variational principles to give different results is identified. The second ansatz keeps the density matrix block diagonal among equivalent orbitals, in a generalization of the method of G. Worth, J. Chem. Phys. **112**, 8322 (2000). The methods perform well in calculating the dynamics of Be and BC^{2+} subject to ultrafast, ultrastrong lasers in severely truncated Hilbert spaces, although they exhibit differing degrees of numerical stability as implemented.

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I. INTRODUCTION

The multiconfiguration time-dependent Hartree-Fock (MCTDHF) method has been pursued [1–18] with the goal of calculating nonpertubative electronic dynamics of molecules in strong fields, in support of experiments using ultrafast laser pulses. The method without permutation symmetry, MCTDH, has been applied with great success over the past two decades to the problem of nuclear dynamics of molecules on coupled Born-Oppenheimer potential energy surfaces [19–25], and there is now a mature effort to apply the method for bosons, MCTDHB [26–31], to problems involving cold atoms in particular.

Because the MCTD(H/HF/HB) methods find use in different physical contexts, the realities accessory to their numerical implementation are considerably different. However, the working equations for MCTDHF and MCTDHB are simply those of MCTDH, accounting for the permutation symmetry of the wave function. All of these methods describe the wave function as a time-dependent linear combination of properly symmetrized time-dependent product basis functions; for MCTDHF these basis functions are Slater determinants.

When total spin S is a good quantum number, linear combinations of determinants that are eigenvectors of $\hat{S}^2$ are used as N-electron basis functions. These spin adapted linear combinations are called "configurations." Otherwise, "configuration" means "Slater determinant."

The difference between MCTDHF and time-dependent configuration interaction is that in MCTDHF, not only are the coefficients multiplying the configurations time-dependent, but so are the configurations themselves. MCTDHF is time-dependent multiconfiguration self-consistent field.

For four electrons,

$$|1236(t)\rangle \equiv \tilde{a}_1^\dagger(t)\tilde{a}_2^\dagger(t)\tilde{a}_3^\dagger(t)\tilde{a}_6^\dagger(t)|0\rangle \qquad (1)$$

is the Slater determinant in which the 1st, 2nd, 3rd, and 6th spin orbitals are occupied; $\tilde{a}^\dagger$ and $\tilde{a}$ create and annihilate spin orbitals. It might be combined with $|1245\rangle$ to to create a singlet or triplet configuration. The MCTDHF wave function ansatz may be written in general as a sum of such determinants,

$$|\Psi(t)\rangle = \sum_a A_a(t)\,|\vec{n}_a(t)\rangle \quad . \qquad (2)$$

For time-dependent configuration interaction, the Slater determinants $|\vec{n}\rangle$ have no time dependence. In that case, Ψ is linear in its parameters $\vec{A}$ and large-scale linear algebra methods can be used for its propagation. The introduction of time dependence into the orbitals, with MCTDHF, makes the problem highly nonlinear.

The term "full configuration interaction" ("full CI") means that all possible Slater determinants that may be formed from a given set of spatial orbitals are included in the basis set. In practice, the term is used even when symmetries of spin and space are accounted for. The number of configurations used in an explicit full configuration interaction calculation becomes prohibitive with modern technology for spaces with large (10 or more) electrons in tens of orbitals. We have recently published [32] a converged calculation of stimulated X-Ray Raman in the NO molecule at 10^{17} W cm^{-2} using 392040 Slater determinants. This is the limit of what we can fit in memory on a single supercomputer node (64GB memory) without using a slower, "direct CI" mode. The largest full configuration interaction calculation we have performed with the implementation [17] is on the Fluorine atom, 19 orbitals, 5 million Slater determinants.

We use the term restricted configuration space to refer to any departure from full configuration interaction. For a configuration interaction calculation with a restricted configuration space, some Slater determinants in the full CI list are simply discarded. Other representations, such as coupled cluster or some treatments using the graphical unitary group [33] also use a subset of the full configuration space, as per an effective parameterization, and we consider them to be restricted configuration space treatments as well.

The total set of orbitals in general may be divided into sets or "shells" of "equivalent" orbitals. Two orbitals are equivalent if the N-electron Hilbert space is left invariant by any unitary transformation of the pair. It is possible to have a restricted configuration space treatment with no inequivalent orbitals (possibly, with Ref. [33]); but any that explicitly treats different orbitals on different footings, or that is sensitive to the resolution of the orbitals within the space they span, like all that we consider, and like the prescriptions used in quantum chemistry, will. For configuration interaction, the N-electron Hilbert space is the list of configurations included in the calculation. In general, with configuration interaction, inequivalent orbitals belong to shells defined by different restrictions on occupancy. A common ansatz for a restricted configuration space within the field of quantum chemistry is called restricted active space (RAS). CIS and CISD, "configuration interaction with singles and doubles," are subsets of RAS. In RAS, there are four shells of orbitals that can be ordered in terms of occupancy [34],

- 1) Doubly occupied
- 2) Total occupation number $> n_1$
- 3) Arbitrary occupation
- 4) Total occupation number $< n_2$

The simpler complete active space ansatz includes only two shells, doubly occupied and full CI (and is therefore also a subset of RAS).

All of the ansatzes for restricted configuration spaces based on restricted active space (RAS) are motivated by bound state quantum chemistry. The interest here is in wave functions with current. The physical situations interrogated by modern and next-generation ultrafast laser experiments involve the excitation of multiple electrons through multiple metastable and continuum electronic states. It is desirable to have a fully general treatment of restricted configuration spaces, so that the method may be adapted to physical systems of interest (and so that the machinery and equations may be used for representations using coupled cluster or matrix product states, for instance). In particular, calculating dissociation problems, or problems such as interatomic Coulombic decay in which the situation is one of weakly interacting fragments, may require multiple different shells of orbitals on equal footing, that cannot be ordered.

However, the restricted active space (RAS) ansatz may suffice to calculate many phenomena of interest. Ionization is present in experiments performed today that involve high-energy or strong lasers and that measure interesting nonperturbative electronic and nuclear dynamics. Its presence means that the single-electron Hilbert space is fundamentally high dimensional, i.e., that a large number of orbitals will be required within the MCTDHF ansatz to describe ionization into multiple channels of even one but especially more than one simultaneously outgoing electron. In this respect the use of straight or exterior complex coordinate scaling [35–39] plays a major role in reducing the numerical effort involved, allowing the variational flexibility of the ansatz to optimize the wave function near to the nuclei. For the calculation of absorption and emission, the matrix elements are dominated by the part of the wave function near the nuclei. In contrast, the calculation of double ionization amplitudes within the MCTDHF method would surely prove challenging, not only due to the formal issues but also to the inherent problem in the need to explicitly represent the doubly ionized electronic wave function far from the residual core by the MCTDHF expansion. For a double ionization problem, a CISD configuration space would be required, with a large number of orbitals in the "virtual," "doubles" space.

The MCTHDF equations of motion are most straightforward to implement if full configuration interaction is used. The introduction of restricted configuration spaces introduces both formal and numerical issues, neither of which have yet been solved in general. In Ref. [40], a method was used that avoided the inclusion of the orbital rotation terms in the short-time propagation of the wave function, because the attempts to do so in a numerically stable way were unsuccessful.

In this paper we derive two methods for employing restricted configuration spaces within MCTDHF. The task is to define the rates and phases of rotations of orbitals ϕ into one another. The rates and phases of rotation are given by the Hermitian matrix g,

$$g_{\alpha\beta} = \left\langle \phi_\alpha \middle| i\frac{\partial}{\partial t}\phi_\beta \right\rangle \quad . \tag{3}$$

Without a restricted configuration list, with full configuration interaction, there is no constraint on the matrix g; it may be chosen Hermitian, but otherwise arbitrarily, and is generally chosen to be zero.

For restricted configuration spaces, $g_{\alpha\beta}$ between equivalent orbitals may be chosen zero, and what is required is to derive $g_{\alpha\beta}$ for inequivalent α and β.

MCTDHF involves a particular choice of a parameterized wave function, and the use of variational principles to define equations of motion for parametrized wave functions has motivated a large amount of study [41–49]. Two variational principles, that which minimizes the norm of the error in the time derivative of the wave function, due to McLachlan [43], and that which conserves energy for time-independent Hamiltonians [45], alternatively called *the* time-dependent variational principle [45, 49] or the Lagrangian variational principle [47], are equivalent in the case of MCTDHF with full configuration interaction. The two principles are collectively referred to as the Dirac-Frenkel [41, 42] variational principle when they are equivalent, not in conflict. Discussion of these issues can be found especially in Refs. [47, 48].

We are not alone in pursuing the use of restricted configuration spaces within MCTDHF; there has recently been a large amount of work on the subject [10–16].

Most of the current implementations of MCTDHF using restricted configuration spaces employ restricted active space (RAS) representations [10, 13–16]. A discussion of the use of complete active space (CAS) with MCTDHF is found in Section IV in Ref. [11]. In Refs. [11, 12] the Lagrangian variational principle was applied to the case of a wave function with fixed configuration coefficients. Refs. [13, 16] also proceed from an explicit statement this principle and not the McLachlan principle.

Kvaal recently described [50] a method for time-dependent coupled cluster that has been employed in calculations of nuclear structure. The formulation and related work is reviewed in Refs. [51, 52]. Other work that also uses a Lagrangian variational principle includes Ref. [53]. The issues regarding variational principles described in this work have been confronted by these authors. However, the solution to these issues derived in Ref. [50] is different from ours. In Ref. [50], following Arponen [54], a "bivariational" treatment is used in which $\langle\Psi|$ is considered independent of $|\Psi\rangle$. The space of variational parameters is enlarged. This is arguably a departure from the MCTDHF ansatz. Ref. [50] states, "This relaxation of orthonormality of the orbitals is necessary to ensure that the bivariational functional is complex analytic if the orbitals are to be treated as variational parameters." In Ref. [50] the variational space was expanded to allow the equations to remain analytic; here, we derive nonanalytic working equations, maintaining the MCTDHF wave function ansatz.

With the exception of that coupled cluster work, the two variational principles have not been clearly distinguished in the recent literature on MCTDHF. In particular, the conditions that the restricted configuration list must satisfy in order for them to be different in MCTDHF have, to our knowledge, not yet been described. An equation for the general case has been presented as Eq. (21) in Ref [16], Eq.(32) in Ref. [13], and Eq.(65) in Ref. [11]. However, explicit expressions for the elements of the matrix g were derived only in a piecewise manner, for the chosen restricted spaces.

We present working equations for the general case, for either variational principle. For a restricted active space (RAS) configuration list with MCTDHF, within the configuration interaction representation, we show that the two variational principles, McLachlan and Lagrangian, are equivalent. For the configuration interaction representation, with an arbitrary restricted configuration space, if any single excitation $\alpha \rightarrow \beta$ corresponds both to one or more transitions from an included configuration to an excluded, and to one or more from an excluded to an included, then the principles are inequivalent.

We also investigate a method in which we abandon the Dirac-Frenkel variational principle, and choose another constraint to determine the evolution of the orbitals. We require that the density matrix be kept block diagonal, with respect to the blocks of equivalent orbitals. Such a prescription has been used in electronic structure [55]. This is a generalization of the method of Ref. [40], MCTDH with selected configurations (S-MCTDH); in that method, the density matrix is kept fully diagonal.

The purpose of this effort is to permit the use of large numbers of orbitals in the MCTDHF expansion. In contrast, the calculations in this paper use few orbitals. We seek the most stringent test of the derived equations and the numerical implementation. It would have been counterproductive to attempt to converge the present calculations, which employ lasers of duration and intensity far beyond the limits of present technology, whose effect is the total destruction of the target system, with respect to the number of orbitals. By truncating the one-electron Hilbert space and using a powerful laser pulse, we force the N-electron Hilbert space that the restricted configuration list spans to evolve rapidly with time. We ensure that there are parts of the one-electron Hilbert space that rotate from one shell of equivalent shell of orbitals to another, or to the excluded space, and back again, during the course of the propagation. The full configuration interaction calculation is substantially in error, and we desire to best represent that wave function with a subset of the already meager N-electron basis.

We begin in Sec. II by presenting the MCTDHF equations as they have been previously derived, with the matrix g left undetermined. In Sections III and IV we present the two different methods we have implemented for determining the matrix g. The results are collected in Sec. V and we conclude in Sec. VI.

II. WORKING EQUATIONS FOR MCTDHF WITH FULL CONFIGURATION INTERACTION

The MCTDHF working equations have been formulated previously [1–5]. They are equivalent to those of MCTDH, the method without permutation symmetry, the derivation of which is presented in e.g. Ref. [20, 21, 23], but in their notation they account for the antisymmetry of the wave function and the single set of orbitals. In all that follows, spin notation is suppressed for simplicity. The subscripts on the creation and annihilation operators, the α and β in $a^\dagger_\beta a_\alpha$, label the spatial orbitals. (To account for spin, consider the creation and annihilation operators to be defined as 1×2 and 2×1 matrices, row and column vectors, respectively. For example,

$$a_4^\dagger \equiv \left(\tilde{a}_7^\dagger \;\; \tilde{a}_8^\dagger \right) \quad a_3 \equiv \begin{pmatrix} \tilde{a}_5 \\ \tilde{a}_6 \end{pmatrix} \quad \langle \vec{x}|\tilde{a}_5^\dagger|0\rangle = \phi_3(\vec{x}) \otimes |{\downarrow}\rangle \tag{4}$$

In this paper these rank-two $(2s+1=2)$ creation and annihilation operators always appear dotted together as transition operators $a^\dagger_\beta a_\alpha$.)

MCTDHF begins with an expansion of the electronic wave function in Slater determinants of time-dependent orbitals, per Eq.(2). The orbitals are expanded in a set of time-independent basis functions f_j,

$$\phi_\alpha(\vec{r},t) = \sum_j c_{j\alpha}(t) f_j(\vec{r}) \ . \tag{5}$$

The MCTDHF equations are derived from the Dirac-Frenkel variational principle, which requires that the expectation value of $H - i\frac{\partial}{\partial dt}$ be stationary with respect to variations of the wave function on the left hand side:

$$\begin{aligned} \forall_{i\alpha} \quad & \left\langle \frac{\partial}{\partial c_{i\alpha}} \Psi(t) \middle| H - i\frac{\partial}{\partial t} \middle| \Psi(t) \right\rangle = 0 \\ \forall_{a} \quad & \left\langle \frac{\partial}{\partial A_a} \Psi(t) \middle| H - i\frac{\partial}{\partial t} \middle| \Psi(t) \right\rangle = 0 \end{aligned} \tag{6}$$

with the constraint that the orbitals remain orthonormal,

$$\langle \phi_\alpha | \phi_\beta \rangle - \delta_{\alpha\beta} = 0 \tag{7}$$

Where $\langle | \rangle$ is the Hermitian inner product.

For full configuration interaction, the wave function is invariant with respect to rotations among the orbitals, which may be compensated for by rotations among the A-coefficients. The solution of Eq.(6) is therefore not uniquely defined, and the matrix g is unconstrained and may be chosen arbitrarily. The simplest way to proceed is to set g to zero. For the orbitals one obtains the equation of motion

$$i\frac{\partial}{\partial t}\vec{c}_\alpha = \sum_\beta \left[(\mathbf{1} - \mathbf{P}) \left[\mathbf{h^{(1)}} \delta_{\alpha\beta} + \sum_\gamma \rho^{-1}_{\alpha\gamma} \widetilde{\mathbf{W}}^{\gamma\beta} \right] + g_{\alpha\beta} \right] \vec{c}_\beta \ , \tag{8}$$

where the projector $\mathbf{P}$ is the matrix representation of the projection operator, $\hat{P} = \sum_\alpha |\phi_\alpha(t)\rangle\langle\phi_\alpha(t)|$, onto the space spanned by the orbitals at time t,

$$\mathbf{P}_{j,j'} = \sum_\alpha c_{j\alpha}(t)\, c_{j'\alpha}(t)^* \ , \tag{9}$$

so that $\mathbf{1} - \mathbf{P}$ projects on to the space orthogonal to that spanned by the orbitals. Our convention is that boldface symbols are matrices in either the orbital ($\vec{c}$) or configuration ($\vec{A}$) basis, whereas regular font denotes scalars. In Eq. (8), $\rho_{\alpha\gamma}$ is the reduced one-electron density matrix element for the wave function in Eq. (2),

$$\rho_{\alpha\beta} = \sum_{ab} A^*_a A_b \langle \vec{n}_a | a^\dagger_\alpha \, a_\beta | \vec{n}_b \rangle \quad , \tag{10}$$

and $\mathbf{h^{(1)}}$ contains the one-electron matrix elements. All quantities in Eq. (8) are time-dependent except for the identity and Kronecker delta. The reduced two-electron operator $\widetilde{\mathbf{W}}$ is defined [2] by the reduced two-particle density matrix, $\Gamma_{\gamma s\alpha l}$ and the reduced potential, $\mathbf{W}_{sl}$,

$$\begin{aligned} \widetilde{\mathbf{W}}^{\gamma\beta} &= \sum_{sl} \Gamma_{\gamma s\alpha l} \mathbf{W}_{sl}(t) \ , & (11) \\ \mathbf{W}_{sl}(t) &= \int \phi^*_s(\vec{r}_2,t) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_l(\vec{r}_2,t) d\vec{r}_2 \ . & (12) \end{aligned}$$

The equations of motion for the A-coefficients are

$$i\frac{\partial}{\partial t}\vec{A} = (\mathbf{H} - \boldsymbol{\tau})\,\vec{A} \qquad \begin{aligned} \mathbf{H}_{a,a'} &= \langle \vec{n}_a | H | \vec{n}_{a'} \rangle \\ \boldsymbol{\tau}_{a,a'} &= \left\langle \vec{n}_a \middle| i\frac{\partial}{\partial t} \vec{n}_{a'} \right\rangle \end{aligned} \tag{13}$$

The matrix $\boldsymbol{\tau}$ is assembled from g just as the one-electron operator part of $\mathbf{H}$ is assembled from its orbital matrix elements; so for full configuration interaction, if g is chosen zero as usual, $\boldsymbol{\tau}$ is zero.

III. RESTRICTED CONFIGURATION SPACES WITH DIRAC-FRENKEL VARIATIONAL PRINCIPLE CONSTRAINT

In this section we treat the problem of the variational formulation of MCTDHF with restricted configuration spaces, which should be viewed as the completion of the true MCTDHF working equations. However, such a prescription, continuing to use the Dirac-Frenkel variational principle to determine g, is not necessarily the best. While one might lose the variational property of energy conservation or minimum norm instantaneous error, there is nothing that says the accuracy of the final wave function would not be superior with another ansatz. Another treatment might be more numerically stable. We note that an ingenious MCTD(H/HF/HB) method has been described [56] in which correlated components are eliminated. The error suffers in the short term, but over the long term yields superior wave functions.

A. Variational principles

As described in the introduction there is a large body of work on the use of variational principles to propagate parameterized wave functions [41–49]. With the introduction of restricted configuration spaces into MCTDHF, there arises a distinction between the two main variational principles. Considering a parameterized wave function $\Psi(\vec{p}(t))$, with derivatives

$$|\Psi_i(\vec{p})\rangle \equiv \frac{\partial}{\partial p_i} |\Psi(\vec{p})\rangle \tag{14}$$

The term “Dirac-Frenkel variational principle” [41, 42] is understood to mean

$$\forall_i \quad \left\langle \Psi_i(\vec{p}(t)) \middle| H - i\frac{\partial}{\partial t} \middle| \Psi(\vec{p}(t)) \right\rangle = 0 \tag{15}$$

As thereby written, for such a parameterized wave function, it is the union of two variational principles [48], the McLachlan variational principle [43], which minimizes the norm of the error of $\frac{\partial}{\partial t}\Psi$,

$$\forall_i \quad \frac{\partial}{\partial \dot{p}_i}\left| H\left|\Psi(\vec{p}(t))\right\rangle - i\sum_j \left|\Psi_j(\vec{p}(t))\right\rangle \dot{p}_j \right|^2 = 0 \quad (16)$$

$$\dot{p}_i \equiv \frac{\partial}{\partial t}p_i(t)$$

and the Lagrangian or the time-dependent variational principle [45], which conserves the expectation value of the energy for time-independent Hamiltonians.

For a parameterized wave function $\Psi(\vec{p}(t))$ the McLachlan or minimum-norm variational principle is equivalent to

$$\forall_i \quad \mathrm{Im}\left\langle \Psi_i(\vec{p}(t)) \middle| H - i\frac{\partial}{\partial t} \middle| \Psi(\vec{p}(t)) \right\rangle = 0 \qquad (17)$$

and the Lagrangian variational principle is equivalent to

$$\forall_i \quad \mathrm{Re}\left\langle \Psi_i(\vec{p}(t)) \middle| H - i\frac{\partial}{\partial t} \middle| \Psi(\vec{p}(t)) \right\rangle = 0 \qquad (18)$$

and thus the Dirac-Frenkel variational principle is the union of the two variational principles.

However, either these variational principles are equivalent, or they are in conflict and cannot be simultaneously satisfied. The eponym "Dirac-Frenkel" should be used when the principles are equivalent; otherwise either McLachlan or Lagrangian/TDVP should be specified. Discussion of these points can be found in e.g. Refs. [47, 48]. In Ref. [48], it is stated that if for every real-valued parameter p_i there exists another real-valued parameter p_j such that

$$i\frac{\partial}{\partial p_i}\Psi(\vec{p}) = \frac{\partial}{\partial p_j}\Psi(\vec{p}) \qquad (19)$$

then the principles are equivalent. This requirement of "complementarity," Eq.(18) in that paper, is meant to hold for variations of parameters that are consistent with any other constraints that may have been placed on the parameter set as a whole. The constraint of orthonormality upon the orbitals in MCTDHF destroys the complementarity between the real and imaginary parts of the orbital coefficients. For full configuration interaction, rotations among the orbitals can be accomplished by rotating the configuration coefficients, so complementarity is restored. One of the main findings of this work is that if any single excitation $\alpha \rightarrow \beta$ corresponds both to at least one transition from an included configuration to an excluded, and to at least one from an excluded to an included, then the principles are inequivalent for MCTDHF with orbitals orthonormal under the Hermitian inner product.

For the preparation of initial eigenfunctions using imaginary time propagation – "cooling" or "relaxation" – we use

$$\forall_i \quad \mathrm{Re}\left\langle \Psi_i(\vec{p}(\tau)) \middle| H + \frac{\partial}{\partial \tau} \middle| \Psi(\vec{p}(\tau)) \right\rangle = 0 \qquad (20)$$

Thus, if the Lagrangian, energy-conserving variational principle is chosen to propagate the wave function, an eigenfunction cooled to a stationary state (g=0) will remain stationary under propagation. If the McLachlan, minimum norm variational principle is chosen, the relaxed solution in general will not be stationary, $g \neq 0$, when propagated forward in real time.

We have observed issues of symmetry breaking when preparing eigenfunctions by relaxation using restricted configuration spaces. We have not found mention of these issues in the literature on multiconfiguration self-consistent field methods in quantum chemistry. Symmetry broken orbitals occur in trivial model systems. For instance, if the two-electron interaction is made attractive, the simplest possible configuration interaction with single excitations (CIS) calculation, using the configuration list $\{|12\rangle,\ |14\rangle\}$ for singlet H_2, yields the same totally symmetric real-valued wave function as that obtained using the generalized valence bond (GVB) configuration list $\{|12\rangle,\ |34\rangle\}$, but with symmetry-broken complex valued orbitals. We believe it is prudent to constrain the cooled orbitals to be real-valued, although doing so may introduce instabilities upon propagation. If orbitals are allowed to be complex, in general, we suspect that this will lead to complex-valued and symmetry broken eigenfunctions, and have observed this to be so in model systems. This issue is not pertinent to the eigenfunctions calculated for the present work; their orbitals were observed to be real-valued upon convergence of the relaxation procedure.

B. Conventions

We have summarized the derivation of MCTDHF for full configuration interaction in Sec. II. The remaining task is to determine elements of the orbital rotation matrix $g_{\alpha\beta}$ by taking variations of the orbitals within the space they span. For full configuration interaction, g is undetermined and may be set to zero. In no case is it necessary to determine the diagonal elements, which may be set to zero because the multiplication of an orbital by a complex factor may always be compensated for by dividing Slater determinants that contain it by that factor.

As can be seen below, in the simplest cases, including restricted active space (RAS), the Hermiticity of the time derivative matrix $g_{\alpha\beta}$ need not be imposed, because only the elements of $g_{\alpha\beta}$ above the diagonal, not those below, are determined and so $g_{\alpha\beta}$ may be chosen Hermitian, without choosing between McLachlan and Lagrangian variational principles, satisfying both. In the general case, if an excitation $\alpha \rightarrow \beta$ may correspond both to an excitation from the included space to the excluded, and to one from the excluded to the included, the Hermiticity must be imposed as a constraint, and the variational principles are inequivalent.

Included configurations are denoted $|\vec{n}_a\rangle$, and the excluded by $|\vec{x}_A\rangle$; the union of these sets is full configuration interaction.

C. Derivation sufficient for restricted active space

As in the standard method, variations on the left hand side with respect to configuration coefficients A_a

$$\frac{\partial}{\partial A_a} |\Psi\rangle = |\vec{n}_a\rangle \tag{21}$$

yield Eq. (13) via the stationary condition

$$\forall_a \qquad 0 = \sum_b \left(\langle \vec{n}_a | H - i\frac{\partial}{\partial t} | \vec{n}_b \rangle - \delta_{ab}\, i\frac{\partial}{\partial t} \right) A_b \tag{22}$$

What remains is to take variations of the orbital coefficients $c_{i\alpha}$. To do so we first separate the time dependence of the A-coefficient:

$$\begin{aligned} &\left\langle \delta\Psi \middle| H - i\frac{\partial}{\partial t} \middle| \Psi \right\rangle = \\ &\qquad \sum_{ab} A_a^* A_b \left\langle \delta\vec{n}_a \middle| H - i\frac{\partial}{\partial t} \middle| \vec{n}_b \right\rangle - i \sum_{ab} A_a^* \frac{\partial}{\partial t} A_b \left\langle \delta\vec{n}_a \middle| \vec{n}_b \right\rangle \end{aligned} \tag{23}$$

Using Eq. 22 and the definition of $\boldsymbol{\tau}$, the last term in Eq.(23) can be manipulated,

$$\begin{aligned} i\sum_{ab} A_a^* \frac{\partial}{\partial t} A_b \, \langle \delta\vec{n}_a | \vec{n}_b \rangle &= \sum_{abc} A_a^* A_c \left(H_{bc} - \tau_{bc} \right) \, \langle \delta\vec{n}_a | \vec{n}_b \rangle \\ &= \sum_{abc} A_a^* A_c \, \langle \delta\vec{n}_a | \vec{n}_b \rangle \left\langle \vec{n}_b \middle| H - i\frac{\partial}{\partial t} \middle| \vec{n}_c \right\rangle \\ &= \sum_{ac} A_a^* A_c \left\langle \delta\vec{n}_a \middle| P^{(N)} \left(H - i\frac{\partial}{\partial t} \right) \middle| \vec{n}_c \right\rangle \\ &\quad - \sum_{aBc} A_a^* A_c \, \langle \delta\vec{n}_a | \vec{x}_B \rangle \left\langle \vec{x}_B \middle| H - i\frac{\partial}{\partial t} \middle| \vec{n}_c \right\rangle \end{aligned} \tag{24}$$

Again, we denote the configurations included in the calculation $|\vec{n}\rangle$, and the excluded $|\vec{x}\rangle$. The projector $P^{(N)}$ acts on all N degrees of freedom and projects onto the full CI space,

$$P^{(N)} = \sum_a |\vec{n}_a\rangle\langle\vec{n}_a| + \sum_A |\vec{x}_A\rangle\langle\vec{x}_A| \tag{25}$$

We thereby arrive at the expression

$$\begin{aligned} &\left\langle \delta\Psi \middle| H - i\frac{\partial}{\partial t} \middle| \Psi \right\rangle \\ &\quad = \sum_{ab} A_a^* A_b \left\langle \delta\vec{n}_a \middle| (1 - P^{(N)}) \left(H - i\frac{\partial}{\partial t} \right) \middle| \vec{n}_b \right\rangle \\ &\quad + \sum_{aBc} A_a^* A_c \, \langle \delta\vec{n}_a | \vec{x}_B \rangle \left\langle \vec{x}_B \middle| H - i\frac{\partial}{\partial t} \middle| \vec{n}_c \right\rangle \end{aligned} \tag{26}$$

To proceed with the derivation, we must explicitly resolve the space of variations of Slater determinants $\langle \delta\vec{n}|$ that are allowed, given the constraint of orthonormality upon the orbitals. We must consider all linearly independent variations of these Slater determinants consistent with that constraint.

The derivation of the MCTDHF equations, as previously described [2], accounts for the the variations of the orbitals that are orthogonal to the orbitals, and results in Eqs. (8) and (13). In the case of full configuration interaction the derivation is finished, because the matrix of time derivatives g is undetermined and may be chosen arbitrarily. Otherwise, one must account for the variations of the orbitals that correspond to a unitary transformation among the orbitals. Those variations are defined in terms of a functional derivative. For a function $f(\vec{c}_1, \vec{c}_2, ...)$ of the orbital coefficients, the functional derivative is

$$\frac{\delta}{\delta\alpha\beta} f \equiv \lim_{\epsilon\rightarrow 0} \frac{\begin{array}{c} f(\vec{c}_1, ...\vec{c}_{\alpha-1}, \vec{c}_\alpha + \epsilon\vec{c}_\beta ...) \\ - f(\vec{c}_1, ...\vec{c}_{\alpha-1}, \vec{c}_\alpha - \epsilon\vec{c}_\beta ...) \end{array}}{2\epsilon} \tag{27}$$

For the Slater determinant basis,

$$\frac{\delta}{\delta\alpha\beta} |\vec{n}_a\rangle = a^\dagger_\beta a_\alpha |\vec{n}_a\rangle \tag{28}$$

so that the stationary condition may be evaluated from Eq.(26) as

$$\begin{aligned} \forall_{\alpha\beta} \quad &\left\langle \frac{\delta}{\delta\alpha\beta} \Psi \middle| H - i\frac{\partial}{\partial t} \middle| \Psi \right\rangle = \\ &0 = \sum_{aBc} A_a^* A_c \, \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{x}_B \rangle \left\langle \vec{x}_B \middle| H - i\frac{\partial}{\partial t} \middle| \vec{n}_c \right\rangle \end{aligned} \tag{29}$$

With

$$\frac{\partial}{\partial t} |\vec{n}_a\rangle = \sum_{\gamma\delta} a^\dagger_\gamma a_\delta |\vec{n}_a\rangle \langle \phi_\gamma | \frac{\partial}{\partial t} \phi_\delta \rangle = \sum_{\gamma\delta} a^\dagger_\gamma a_\delta |\vec{n}\rangle (-ig)_{\gamma\delta} \,, \tag{30}$$

and

$$\begin{aligned} Q_B &\equiv \langle \vec{x}_B \,| H |\, \Psi \rangle = \sum_c A_c \, \langle \vec{x}_B \,| H |\, \vec{n}_c \rangle \\ w_{B\alpha\beta} &\equiv \langle \vec{x}_B | a^\dagger_\alpha a_\beta | \Psi \rangle = \sum_c A_c \, \langle \vec{x}_B | a^\dagger_\alpha a_\beta | \vec{n}_c \rangle \end{aligned} \tag{31}$$

Eq.(29) becomes

$$\forall_{\alpha\beta} \quad \sum_{\gamma\delta} (w^\dagger w)_{\alpha\beta\gamma\delta} \, (-ig_{\gamma\delta}) = \; -i(w^\dagger Q)_{\alpha\beta} \tag{32}$$

for propagation; for relaxation,

$$\forall_{\alpha\beta} \quad \sum_{\gamma\delta} (w^\dagger w)_{\alpha\beta\gamma\delta} \, (-ig_{\gamma\delta}) = \; -(w^\dagger Q)_{\alpha\beta} \quad . \tag{33}$$

We solve for the antihermitian matrix $-ig$ and arrange the factors of i in this manner in order to clarify the exposition below. The matrix $-ig$ is simply the matrix of time derivatives $\langle\phi_i|\frac{\partial}{\partial t}|\phi_j\rangle$.

Certain components of this matrix equation may be undetermined. Consider complete active space (CAS), with doubly occupied core orbitals and full configuration interaction in the remaining, "active" orbitals. Consider the orbitals to be numbered such that the core orbitals come first. For such a configuration basis, there are no overlaps $\langle\vec{n}_a|a^\dagger_\alpha a_\beta|\vec{x}_B\rangle$ to consider with $\alpha > \beta$. We thus have the equations $0 = 0$ for the corresponding rows of the matrix equation, which may be satisfied by any choice of the corresponding $g_{\alpha\beta}$. The matrix may be chosen Hermitian, and one is finished. No difference has arisen between the McLachlan and Lagrangian variational principles; they are both satisfied.

In general, for configuration interaction, the criterion that the restricted configuration list must satisfy in order for the matrix g to be able to be chosen Hermitian without accounting for the constraint of orthonormality, making the two variational principles, McLachlan and Lagrangian, equivalent is that for every pair of orbitals α, β for which there exist an excluded configuration A and included configuration a such that $\langle\vec{n}_a|a^\dagger_\alpha a_\beta|\vec{x}_A\rangle$ is nonzero, i.e., for which $\alpha \to \beta$ corresponds to an excitation from an included configuration to an excluded configuration, there are no b and B such that $\langle\vec{x}_B|a^\dagger_\alpha a_\beta|\vec{n}_b\rangle$ is nonzero, i.e., $\beta \to \alpha$ corresponds to no excitation from an included configuration to an excluded configuration.

With restricted active space (RAS), for fermions, since the restrictions on the configuration list are only functions of orbital occupancy, and there is only one shell with minimum occupancy into which electrons can be excited, and only one shell with maximum occupancy from which electrons can be excited, the McLachlan and Lagrangian principles are equivalent. With RAS, as described in the introduction, if $\alpha \to \beta$ corresponds to an excitation from included to excluded, then β is in shell 4 or α is in shell 1 or 2; furthermore β is not in shell 1 because shell 1 is fully occupied in the included RAS configurations. In all of these cases, $\beta \to \alpha$ cannot connect an included configuration to an excluded one. Specifically: If β is in shell 4, then α is not; if α is in shell 2, then β is not, i.e. β is not in shells 1 or 2; either way, the excitation $\beta \to \alpha$ violates none of the constraints on occupation number. If α is in shell 1, there is no excitation $\beta \to \alpha$ to consider.

D. Enforcing Hermiticity of g

In general, the Hermicity of g, $g_{\alpha\beta} = g^*_{\beta\alpha}$, must be enforced, so that the orbitals remain orthonormal. Because the Hermitian dot product ("bra-ket") of two vectors is a nonanalytic function of the coefficients in the bra vector, the variational principles become inequivalent.

To account for the nonanalytic constraint we use real arithmetic. Complex numbers are represented by two-vectors of real numbers, $z \to \{\mathrm{Re}(z), \mathrm{Im}(z)\}$, and operations upon them from the left, including multiplication by complex numbers, are represented by 2x2 matrices [57]. So in a product $abcd$ of complex numbers, consider d to be a 2-vector and a, b, c to be 2x2 matrices. We will write vectors with regular font and matrices with bold font. With this convention, the product would be written $\boldsymbol{abc}d$. The conjugation operator $*$ is the Pauli matrix σ_z. Explicitly,

$$\boldsymbol{1} \equiv \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad \boldsymbol{i} \equiv \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} \quad \boldsymbol{*} \equiv \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{34}$$

Taking a complex-valued matrix equation $AX = B$, it may be solved with real arithmetic as $\boldsymbol{A}X = B$; the complex numbers in A are translated to 2×2 matrices via the definitions of $\boldsymbol{1}$ and $\boldsymbol{i}$ above, and the vectors X and B are now taken to be real vectors with twice their original dimensions, e.g. $A \to \{\mathrm{Re}(A_1), \mathrm{Im}(A_1), \mathrm{Re}(A_2), ...\}$ [57].

Restricting Hermiticity of g reduces the number of unknowns in the system of linear equations. For propagation,

$$\begin{aligned} \forall_{\alpha\beta} \quad \sum_{\gamma<\delta} \left[(\boldsymbol{w}^\dagger\boldsymbol{w})_{\alpha\beta\gamma\delta} - (\boldsymbol{w}^\dagger\boldsymbol{w})_{\alpha\beta\delta\gamma}\boldsymbol{*}\right](-\boldsymbol{i}g_{\gamma\delta}) \\ = -\boldsymbol{i}(\boldsymbol{w}^\dagger Q)_{\alpha\beta} \end{aligned} \tag{35}$$

For relaxation, the left hand side has a factor of (-1) not $(-i)$. This equation may be simplified using the rectangular matrix – defined only for $\gamma < \delta$ but both $\alpha < \beta$ and $\alpha > \beta$ –

$$\boldsymbol{T}_{\alpha\beta\gamma\delta} = \delta_{\alpha\gamma}\delta_{\beta\delta}\boldsymbol{1} - \delta_{\alpha\delta}\delta_{\beta\gamma}\boldsymbol{*} \tag{36}$$

yielding

$$\forall_{\alpha\beta} \quad \sum_{\gamma<\delta}(\boldsymbol{w}^\dagger\boldsymbol{w}\boldsymbol{T})_{\alpha\beta\gamma\delta}(-\boldsymbol{i}g_{\gamma\delta}) = -\boldsymbol{i}(\boldsymbol{w}^\dagger Q)_{\alpha\beta} \tag{37}$$

We now have a greater number of equations than unknowns. To proceed with the Dirac-Frenkel derivation we must account for the constraint of orthonormality of the orbitals in considering the variations on the left hand side. We do not permit orbitals to evolve as

$$\phi_i(t+\delta) = \phi_i(t) + \sum_j \epsilon_{ij}\phi_j \tag{38}$$

with arbitrary ϵ_{ij}; to maintain orthonormality $\epsilon_{ij} = -\epsilon^*_{ji}$. The allowed variations of the wave function within the space spanned by the orbitals are thus

$$\Psi(t+\delta) = \Psi(t) + \epsilon\left(a^\dagger_\alpha a_\beta - a^\dagger_\beta a_\alpha\right)\Psi(t) \tag{39}$$

and

$$\Psi(t+\delta) = \Psi(t) + i\epsilon\left(a^\dagger_\alpha a_\beta + a^\dagger_\beta a_\alpha\right)\Psi(t) \tag{40}$$

with ϵ a real-valued infinitesimal. Defining

$$\begin{aligned}
\Big|\frac{\delta}{\delta(\alpha\beta)_r}\Psi\Big\rangle &\equiv \Big|\frac{\delta}{\delta\alpha\beta}\Psi\Big\rangle - \Big|\frac{\delta}{\delta\beta\alpha}\Psi\Big\rangle \\
&= \left(a^\dagger_\alpha a_\beta - a^\dagger_\beta a_\alpha\right)|\Psi\rangle \\
\Big|\frac{\delta}{\delta(\alpha\beta)_i}\Psi\Big\rangle &\equiv i\Big|\frac{\delta}{\delta\alpha\beta}\Psi\Big\rangle + i\Big|\frac{\delta}{\delta\beta\alpha}\Psi\Big\rangle \\
&= i\left(a^\dagger_\alpha a_\beta + a^\dagger_\beta a_\alpha\right)|\Psi\rangle \quad ,
\end{aligned} \tag{41}$$

the statement of the Lagrangian, "time-dependent," or energy-conserving variational principle is thus

$$\begin{aligned}
&\forall_{\alpha<\beta} \quad \mathrm{Re}\Big\langle\frac{\delta}{\delta(\alpha\beta)_r}\Psi\Big|H - i\frac{\partial}{\partial t}\Big|\Psi\Big\rangle = 0 \\
&\forall_{\alpha<\beta} \quad \mathrm{Re}\Big\langle\frac{\delta}{\delta(\alpha\beta)_i}\Psi\Big|H - i\frac{\partial}{\partial t}\Big|\Psi\Big\rangle = 0
\end{aligned} \tag{42}$$

and the McLachlan or minimum norm error principle takes the imaginary parts,

$$\begin{aligned}
&\forall_{\alpha<\beta} \quad \mathrm{Im}\Big\langle\frac{\delta}{\delta(\alpha\beta)_r}\Psi\Big|H - i\frac{\partial}{\partial t}\Big|\Psi\Big\rangle = 0 \\
&\forall_{\alpha<\beta} \quad \mathrm{Im}\Big\langle\frac{\delta}{\delta(\alpha\beta)_i}\Psi\Big|H - i\frac{\partial}{\partial t}\Big|\Psi\Big\rangle = 0
\end{aligned} \tag{43}$$

Placing the equations for variations $\partial(\alpha\beta)_r$ in the odd-numbered rows of the resulting real valued matrix equation, and those for $\partial(\alpha\beta)_i$ in the even-numbered rows, Eq. (42) is written

$$\forall_{\alpha<\beta} \quad \sum_{\gamma\delta} \mathbf{T}_{\gamma\delta\alpha\beta} \begin{pmatrix} \mathrm{Re}\ \langle\Psi|(a^\dagger_\delta a_\gamma)(H - i\frac{\partial}{\partial t})|\Psi\rangle \\ \mathrm{Im}\ \langle\Psi|(a^\dagger_\delta a_\gamma)(H - i\frac{\partial}{\partial t})|\Psi\rangle \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{44}$$

and one then obtains the real-valued antisymmetric matrix equation

$$\forall_{\alpha<\beta} \quad \sum_{\gamma<\delta} (\boldsymbol{T}^\dagger \boldsymbol{i}\boldsymbol{w}^\dagger \boldsymbol{w}\boldsymbol{T})_{\alpha\beta\gamma\delta}(-\boldsymbol{i}g_{\gamma\delta}) = (\boldsymbol{T}^\dagger \boldsymbol{w}^\dagger Q)_{\alpha\beta} \tag{45}$$

for the Lagrangian, "time-dependent," or energy-conserving variational principle. Note that $\boldsymbol{T}$ and $\boldsymbol{i}$ do not commute but $\boldsymbol{i}$ and $\boldsymbol{w}$ are both complex numbers and so commute. Similarly, the McLachlan or minimum norm error variational principle, Eq. (43), may be written as a real-valued symmetric matrix equation as

$$\forall_{\alpha<\beta} \quad \sum_{\gamma<\delta} (\boldsymbol{T}^\dagger \boldsymbol{w}^\dagger \boldsymbol{w}\boldsymbol{T})_{\alpha\beta\gamma\delta}(-\boldsymbol{i}g_{\gamma\delta}) = -(\boldsymbol{T}^\dagger \boldsymbol{i}\boldsymbol{w}^\dagger Q)_{\alpha\beta} \tag{46}$$

Eqs. (46) and (45) are the final working expressions used here. They apply regardless of permutation symmetry.

The issue of integrating the MCTDHF equations is entirely a numerical one. It is not clear *a priori* which variational principle will perform better in actual calculations, especially as treated within an ad hoc mean field implementation such as that used here [17].

It is not unreasonable to guess that some combination of the two methods may provide the most stable result. While the McLachlan and Lagrangian variational principles may not be simultaneously satisfied for general restricted spaces, it is trivial to solve the overdetermined system of linear equations that combines them, Eq.(37), in a least-squares manner. Any justification as a variational principle is surely lost in such an ad hoc method. However, as will be demonstrated, Eq. (46) or (45) may be underdetermined at times during a propagation, and therefore must be regularized to be stable for typical mean field time steps. By combining them in an ad hoc manner, the hope is that when one is underdetermined, the other is not, and therefore that the ad hoc combination will result in well determined, stable propagation.

We make an evenly weighted ad hoc combination of the two variational principles by performing the least-norm-error solution of Eq.(37) via singular value decomposition. We also perform calculations in which find the least-norm-error simultaneous solution of Eq. (46), and Eq. (45) times a factor. In this method, one variational principle is dominant, but the other is also included to provide well determined propagation. With a factor of 1, this is equivalent to using Eq.(37). For the calculations shown in section V B, the best method is Lagrangian with 10% McLachlan.

IV. RESTRICTED CONFIGURATION SPACES WITH DENSITY MATRIX CONSTRAINT

In this section we describe the implementation of the constraint that the one electron density matrix be kept block diagonal, an alternative to using the Dirac-Frenkel variational principle to determine g. This ansatz has been used in electronic structure [55]. It is reasonable to think that it would perform well, because it means that the orbitals that occur in a greater number of Slater determinants are kept more highly occupied.

This method is a generalization of the method of Ref. [40], MCTDH with selected configurations (S-MCTDH); in that method, the density matrix is kept fully diagonal, i.e., natural orbitals are propagated, and the restricted configuration list is arbitrary. The corresponding equations for g have been derived in Ref. [23].

If the density matrix begins block diagonal, it may be kept block diagonal by constraining the derivatives of the off-block-diagonal matrix elements to be zero. Since $\langle\vec{n}_a|a^\dagger_\alpha a_\beta|\vec{n}_{a'}\rangle$ is time-independent, the time derivative of the density matrix

$$\rho_{\alpha\beta}(t) = \langle\Psi(t)|a^\dagger_\alpha(t)a_\beta(t)|\Psi(t)\rangle = \sum_{aa'} A^*_a A_{a'} \langle\vec{n}_a|a^\dagger_\alpha a_\beta|\vec{n}_{a'}\rangle \tag{47}$$

is

$$\frac{\partial}{\partial t}\rho_{\alpha\beta} = \sum_{aa'} \left(A^*_a(\frac{\partial}{\partial t}A)_{a'} + A_{a'}(\frac{\partial}{\partial t}A)^*_a \right) \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{n}_{a'} \rangle \tag{48}$$

With Eq.(30) we obtain

$$\left(\frac{\partial}{\partial t} A \right)_a = (-iHA)_a - \sum_{\delta\gamma a''} \langle \vec{n}_a | a^\dagger_\delta a_\gamma | \vec{n}_{a''} \rangle A_{a''} (-i g_{\delta\gamma}) \tag{49}$$

Then

$$\begin{aligned} \frac{\partial}{\partial t}\rho_{\alpha\beta} = \sum_{aa'} \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{n}_{a'} \rangle \Bigg[& (A^*_a(-iHA)_{a'} + A_{a'}(-iHA)^*_a) \\ & + \sum_{\gamma\delta a''} \left(\langle \vec{n}_a | a^\dagger_\gamma a_\delta | \vec{n}_{a''} \rangle A_{a''}(-i g_{\gamma\delta}) \right)^* A_{a'} \\ & + A^*_a \langle \vec{n}_{a'} | a^\dagger_\delta a_\gamma | \vec{n}_{a''} \rangle A_{a''}(-i g_{\delta\gamma}) \Bigg] \end{aligned} \tag{50}$$

In this derivation we do not enforce Hermiticity of g via, for example, real valued linear algebra as in Sec. III. Instead, we demonstrate that the block diagonal density matrix ansatz is consistent with a Hermitian g. We assume Hermitian g in the derivation; the final expression is demonstrably consistent. In contrast, making this assumption at the beginning of the derivation for the McLachlan or Lagrangian variational principles leads to a contradiction in the general case.

The first term of Eq.(50) is defined

$$\kappa_{\alpha\beta} \equiv \sum_{aa'} \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{n}_{a'} \rangle \left(A^*_a(-iHA)_{a'} + A_{a'}(-iHA)^*_a \right) \tag{51}$$

For MCTDHF, the second term may be manipulated,

$$\begin{aligned} & \sum_{aa'} \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{n}_{a'} \rangle \sum_{\gamma\delta a''} \left(\langle \vec{n}_a | a^\dagger_\gamma a_\delta | \vec{n}_{a''} \rangle A_{a''}(-i g_{\gamma\delta}) \right)^* A_{a'} \\ & \quad + A^*_a \langle \vec{n}_{a'} | a^\dagger_\delta a_\gamma | \vec{n}_{a''} \rangle A_{a''}(-i g_{\delta\gamma}) \\ & = \sum_{\gamma\delta a a' a''} \Big[- \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{n}_{a'} \rangle \langle \vec{n}_{a''} | a^\dagger_\delta a_\gamma | \vec{n}_a \rangle A^*_{a''} A_{a'} \\ & \quad + \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{n}_{a'} \rangle \langle \vec{n}_{a'} | a^\dagger_\delta a_\gamma | \vec{n}_{a''} \rangle A^*_a A_{a''} \Big] (-i g_{\delta\gamma}) \\ & = \sum_{\gamma\delta a a''} \Big[- \langle \vec{n}_a | a^\dagger_\delta a_\gamma a^\dagger_\alpha a_\beta | \vec{n}_{a''} \rangle A^*_a A_{a''} \\ & \quad + \langle \vec{n}_a | a^\dagger_\alpha a_\beta a^\dagger_\delta a_\gamma | \vec{n}_{a''} \rangle A^*_a A_{a''} \Big] (-i g_{\delta\gamma}) \\ & \quad + \sum_{\gamma\delta a A' a''} \Big[\langle \vec{n}_a | a^\dagger_\delta a_\gamma | \vec{x}_{A'} \rangle \langle \vec{x}_{A'} | a^\dagger_\alpha a_\beta | \vec{n}_{a''} \rangle A^*_a A_{a''} \\ & \quad - \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{x}_{A'} \rangle \langle \vec{x}_{A'} | a^\dagger_\delta a_\gamma | \vec{n}_{a''} \rangle A^*_a A_{a''} \Big] (-i g_{\delta\gamma}) \\ & = \sum_{\gamma\delta} \Big[\delta_{\delta\beta}\rho_{\gamma\alpha} - \delta_{\gamma\alpha}\rho_{\delta\beta} - (w^\dagger w)_{\beta\alpha\delta\gamma} + (w^\dagger w)_{\gamma\delta\alpha\beta} \Big] \\ & \qquad \times (-i g_{\delta\gamma}) \end{aligned} \tag{52}$$

with w as defined in Eq. (31). We solve the linear equation $\frac{\partial}{\partial t}\rho_{\alpha\beta} = 0$,

$$\begin{aligned} & \forall_{\alpha\beta} \quad \kappa_{\alpha\beta} = \\ & \sum_{\gamma\delta} \Big[\delta_{\delta\beta}\rho_{\alpha\gamma} - \delta_{\gamma\alpha}\rho_{\delta\beta} - (w^\dagger w)_{\beta\alpha\delta\gamma} + (w^\dagger w)_{\gamma\delta\alpha\beta} \Big] (-i g_{\delta\gamma}) \end{aligned} \tag{53}$$

for $-ig$, where α and β, and γ and δ, are inequivalent orbitals. The Hermiticity of g is guaranteed by the Hermiticity of ρ and κ. We solve for both $g_{\alpha\beta}$ and $g_{\beta\alpha}$ and check the Hermiticity.

Note that for complete active space, CAS, the solution is not determined; the density matrix is block diagonal regardless of g. One can see that $\kappa = 0$ and the trivial solution $g = 0$ is allowed. This is an unsatisfactory property of the ansatz. We do not employ CAS in the example on Beryllium below in which we study this density matrix constraint. However, we examine the method in which the density matrix constraint equation appropriate for full configuration interaction is used to determine g for the restricted configuration space calculation. In other words, we modify the working equation, Eq. (53) by eliminating the terms with w and adding the terms for the excluded space to κ:

$$\begin{aligned} \kappa_{\alpha\beta} \rightarrow \kappa_{\alpha\beta} & + \sum_{aA'} \langle \vec{n}_a | a^\dagger_\alpha a_\beta | \vec{x}_{A'} \rangle A^*_a (-iHA)_{A'} \\ & + \sum_{Aa'} \langle \vec{x}_A | a^\dagger_\alpha a_\beta | \vec{n}_{a'} \rangle A_{a'} (-iHA)^*_A \end{aligned} \tag{54}$$

For the Beryllium system calculated, we find that the equations – the correct equation, Eq. (53), and that which would keep the density matrix block diagonal for the full configuration interaction, as described, labeled “denmat FCI” in figures below – perform similarly; the terms by which they differ are clearly small for this case. Therefore it seems that using the full configuration interaction equation for g instead of the one appropriate for the restricted configuration space in question, or some compromise, may be a way to uniquely determine the matrix elements of g involving doubly occupied shells. An optimal treatment of doubly occupied shells within this density matrix ansatz requires additional thought.

V. PERFORMANCE

We compute the dynamics of two systems using restricted configuration spaces with the implementation described in Ref. [17]. We also perform full configuration interaction calculations, which are used to judge the accuracy of the results.

The initial states are obtained by imaginary time relaxation. Three different initial states, full CI, Dirac-Frenkel, and density matrix, are therefore involved. However, with our implementation we can only apply the density matrix treatment to the first calculation, on Be. For

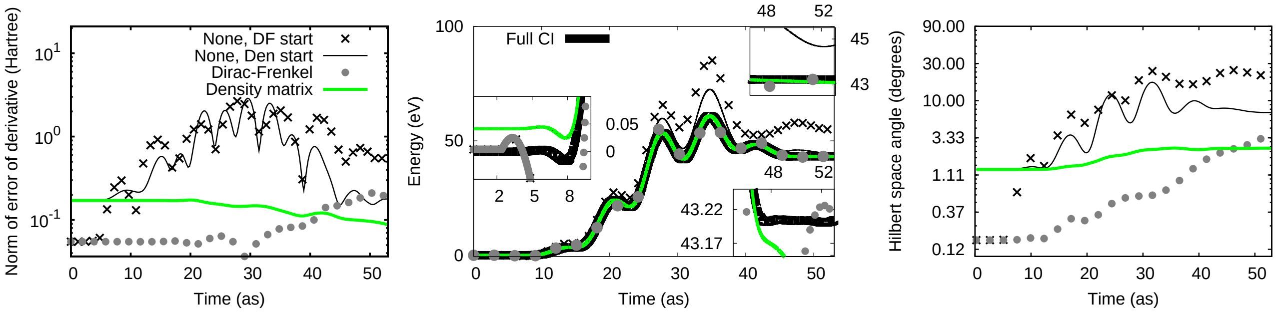

FIG. 1: (Color online) Analysis of propagation for Beryllium test case. The legend in the left panel applies to all of them.

the second calculation the label Dirac-Frenkel is no longer appropriate for the propagation because the McLachlan and Lagrangian variational principles are distinguished. We perform three different propagations of the initial state, corresponding to these two variational principles and their ad hoc combination, as described above.

The energies before and after the pulse for the various calculations are listed in Table I. We have tried to converge the numbers in Table I with respect to the mean field time step. For the other results a time step of 0.01 atomic units is sufficient. They include the norm of the error in the instantaneous derivative, defined as $|QH\Psi|$ with Q the projector onto the configuration space excluded from the calculation, and the expectation value of the energy, $\langle\Psi|H|\Psi\rangle/\langle\Psi|\Psi\rangle$; these quantities are properties of each wave function individually. The restricted configuration wave functions are compared with the full CI wave function by computing their Hilbert space angle, which for two wave functions Ψ and Ψ' is

$$\theta = \cos^{-1}\left(\frac{\langle\Psi|\Psi\rangle + \langle\Psi'|\Psi'\rangle}{2\ |\langle\Psi|\Psi'\rangle|}\right) \quad , \tag{55}$$

and for the BC^{2+} calculation, the norm of the difference, $|\Psi - \Psi'|$.

All pulses have a sine-squared envelope.

A. Neutral Be, X-ray pulse

In order to compare the Dirac-Frenkel and density matrix treatments, we calculate the dynamics of Be subject to a laser pulse with central frequency 272eV, intensity 10^{18} W cm^{-2}, and full duration 53as. We use a radial grid with three finite elements, 3, 6, and 6 a_0 long, complex scaling the final element at an angle of 0.5 radians. We use five orbitals, all with angular momentum projection $m_l = 0$. In the restricted configuration list, we only include configurations in which the combined occupancy of the orbitals that begin as $1s$ and $2s$ is two or more. Full configuration interaction includes 100 Slater determinants, and the restricted configuration space uses 55 of them. With this restricted configuration list the variational principles are equivalent and are therefore referred to as Dirac-Frenkel. In other words the first quadrant ($\alpha < \beta$ in row and column) of Eq.(32) is sufficient; one does not need to choose between Eq.(45) or (46), and if used they produce equivalent results as implemented.

Calculation	Start	Finish	Change
Be Full CI	-14.30475	-12.71702	1.58773
Be Dirac-Frenkel	-14.30460	-12.71675	1.58785
Be Density matrix	-14.30322	-12.72322	1.58000
Be Denmat FCI	-14.30322	-12.72320	1.58002
Be None, DF start	-14.30460	-12.27275	2.03185
Be None, Den start	-14.30322	-12.65978	1.64345
BC^{2+} Full CI	-61.275139	-60.611515	0.663624
BC^{2+} Lagrangian	-61.275135	-60.611508	0.663627
BC^{2+} McLachlan	-61.275135	-60.611208	0.663927
BC^{2+} Combination	-61.275135	-60.611330	0.663805
BC^{2+} None	-61.275135	-60.645813	0.629322

TABLE I: Absolute energies of the wave functions before and after the pulse, in atomic units (Hartree). Be results are calculated using a mean field time step of 0.00002au; those for BC^{2+}, 0.001au. All digits except the last are converged with respect to the mean field time step.

From Fig. 1 one can see that the Dirac-Frenkel constraint produces the closest approximation to the full configuration interaction wave function, during the initial stages of the propagation. The errors in both the derivative of the wave function and the wave function are minimal using the Dirac-Frenkel constraint, until about 45 attoseconds. At the end of the propagation, the density matrix constraint has produced a superior wave function: the final Hilbert space angle is less than that for the Dirac-Frenkel constraint. In the middle panel showing the expectation value of the instantaneous Hamiltonian, and in Table I, one can see that the initial energy of the Dirac-Frenkel constrained wave function is much closer to the full CI value than is that for the density matrix constraint; at the end of the pulse, the Dirac-Frenkel result returns almost exactly to the full CI value. The agreement in the change in energy – the physically rele-

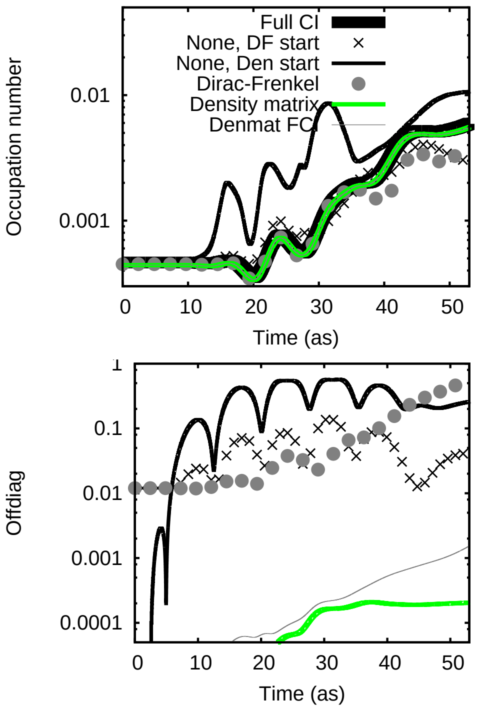

FIG. 2: (Color online) Top panel: occupation of the least occupied (fifth) natural orbital for Beryllium test case. Bottom panel: measure of off-diagonality of the density matrix of Eq. (56). "Denmat FCI" refers to using the equation that would keep the density matrix block diagonal with full configuration interaction, as described at the end of Sec. IV.

vant quantity, the work done by the pulse – is even more remarkable for the Dirac-Frenkel calculation. As can be seen in Table I, the change in energy for Dirac-Frenkel agrees with that for full CI to within 0.2meV; on a relative basis the agreement is five parts in one million. In contrast, the restricted space wave functions propagated with $g = 0$, no constraint, finish with errors of 2 and 8eV, depending upon the initial state chosen. The energy of both of the restricted space wave functions, Dirac-Frenkel and density matrix, are remarkably close to one another and to the full CI result for the duration of the pulse. Whereas the energy ranges over more than 50eV, the full CI and constrained wave functions are always within 0.05eV of one another – except that the density matrix calculation diverges from this range at very end of the calculation.

The smallest of the natural orbital occupation numbers is plotted in the top panel of Fig. 2. The density matrix constraint calculation result is very close to the full CI result. The occupation number from the Dirac-Frenkel constraint calculation begins to deviate from the full CI result near 35as. The behavior of the unrestricted calculation is very different depending on the initial state, with the density matrix initial state occupation number deviating from full CI far more than does that from the Dirac-Frenkel initial state.

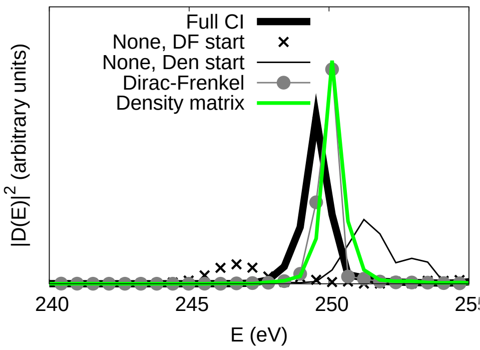

FIG. 3: (Color online) Fourier transform of induced dipole moment for Be calculation obtained after propagation for 7.25fs.

In the bottom panel of Fig. 2 we plot the quantity

$$\texttt{offdiag} = \frac{1}{|\Psi|^2}\sqrt{\sum_{\alpha<\beta,\ \text{different shells}} |\rho_{\alpha\beta}|^2} \qquad (56)$$

as a measure of the degree to which the density matrix is off-block-diagonal. The density matrix constraint is designed to keep the density matrix fully block diagonal, but the mean field treatment and other numerical considerations lead to a nonzero value being accumulated. Interestingly, while both the Dirac-Frenkel and density matrix constraints give good approximations to the full CI solution, the Dirac-Frenkel calculation produces a highly off block diagonal density matrix. In Fig. 2 a mean field time step of 0.0001 atomic units has been used, and there is an observable off diagonal component to the density matrix for the density matrix constraint treatment, rising above the x-axis of the figure just after 20as. This result may be reduced with a smaller time step. Also shown is the result obtained by using the equation that would keep the density matrix block diagonal if the full configuration interaction space were used for the propagation, as described at the end of Sec. IV, labeled "Denmat FCI." This result is converged with respect to the mean field time step as are all the others. As can be seen in Fig. 2 and in Table I, the "Denmat FCI" treatment behaves very similarly to the proper equation, Eq. (53). As discussed in Sec. IV, it has the advantage of making the orbital rotation matrix elements involving doubly occupied orbitals well-determined.

We show the Fourier transform of the dipole moment calculated over an interval of 7.25 fs in Fig. 3. The density matrix and Dirac-Frenkel treatments produce nearly the same result, which is somewhat different from the full CI result, being shifted by about +0.5eV and being slightly more narrow and therefore taller. The calculations performed without one of the constraints manage to produce peaks, but they are much wider, shorter, and substantially shifted from the other results.

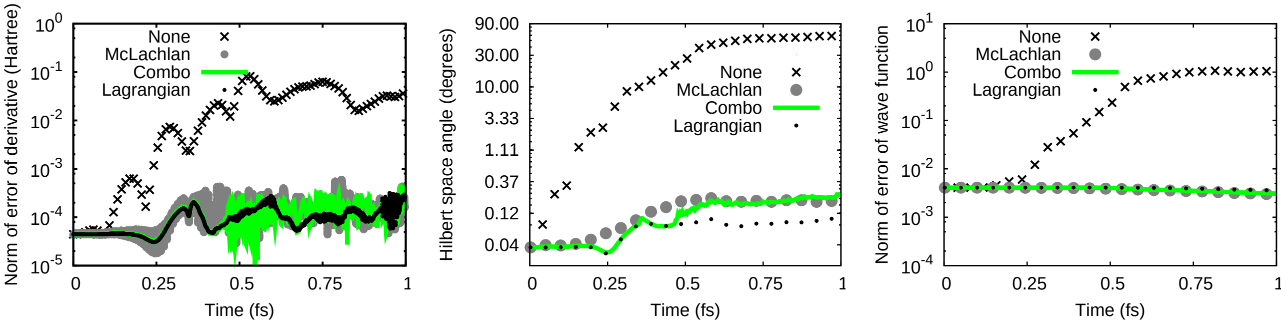

FIG. 4: (Color online) Analysis of propagation for BC^{2+} case.

B. BC^{2+} charge exchange

In order to analyze the performance of the Dirac-Frenkel constraint with arbitrary configuration spaces, for a case in which the McLachlan and Lagrangian variational principles are different, we calculate the dynamics of B^+ and C^+ at $3a_0$ separation, subject to a 1fs, 5×10^{14} W cm^{-2} pulse, with polarization parallel to the bond axis, and central frequency 15.9eV, tuned approximately resonant to the charge exchange transition going to $B + C^{2+}$.

We use five finite elements for the radial degree of freedom ξ in the prolate spheroidal coordinate system, with lengths 1, 3, 3, 6, and 10. The coordinate is unitless; given the internuclear separation of $3a_0$, these elements are approximately 3, 9, 9, 18, and $30a_0$ long. The final three elements are complex scaled at an angle of 0.5 radians. The Hamiltonian has a large antihermitian component and it is important to note that at the end of this calculation, the norm of the wave function as represented by exterior complex scaling has decreased from one to 0.93 due to the absorption of ionized flux. The total amount ionized is likely much larger than 7%; that is only the part that has already been absorbed by 1fs.

We employ a configuration space designed for the interacting particles. There are two shells of orbitals, corresponding to B^+ and C^+ atomic orbitals at large separation. There are three (sigma) orbitals for each fragment. We restrict the number of electrons in either shell to be 4 or 5, permitting B^+ / C^+ and B / C^{2+} charge arrangements. The number of determinants for full CI is 90, of which 72 are included in the restricted configuration list.

This defines a configuration space much different from RAS; we have two shells on equal footing, and therefore for this case the Hermiticity of the g matrix must be enforced and the variational principles become inequivalent. We employ the McLachlan / minimum norm error principle, or the Lagrangian / "time-dependent" / energy-conserving principle, using Eq.(46) or (45), respectively.

We also calculate the result of the ad hoc combination of the two, as described in section III D, which consists of attempting to simultaneously solve both equations. For an evenly weighted combination, we obtain the least-norm-error solution to Eq.(37) using singular value decomposition. For an unevenly weighted combination, the algebra leading to Eqs. (46) and (45) must be performed, and we obtain the least-norm-error solution of both Eq. (46), and Eq. (45) times a factor.

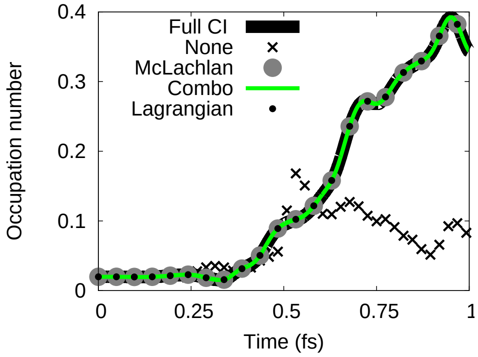

FIG. 5: (Color online) Occupation of the least occupied (sixth) natural orbital for BC^{2+} test case.

We do not have the capability to apply this interacting fragment restricted configuration space to the density matrix constraint treatment, due to our inability to prepare the initial state.

We compare four calculations – full configuration interaction, McLachlan, Lagrangian, and evenly weighted combination – in Table I and Figs. 4 and 5. In Table I, one can again see remarkable agreement in the work done by the pulse, the change in energy. As would be expected, the Lagrangian variational principle, which conserves energy for time-independent Hamiltonians, produces the best agreement, at five parts in one million; the unconstrained calculation disagrees at a 5% level.

In Fig 4 we show the error in the instantaneous derivative, and the norm of the difference and Hilbert space angle relative to the full configuration interaction solution. The former measure is sensitive to phase and the latter is not. All the measures show that all three treatments produce wave functions very close to the full CI result,

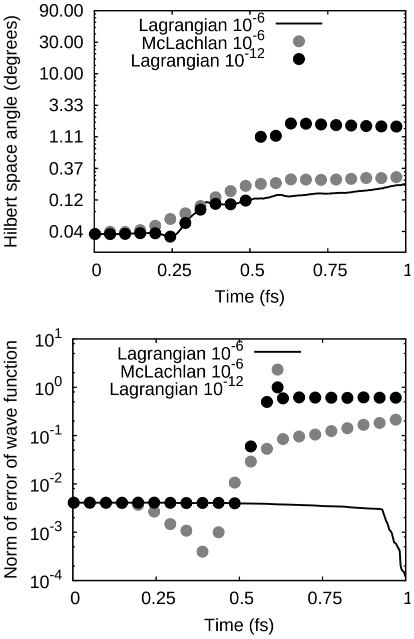

FIG. 6: BC^{2+} propagation with mean field time step 0.01 atomic units and different regularization parameters, as labeled.

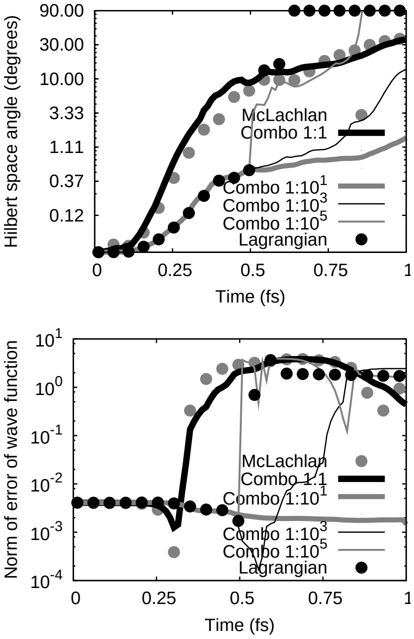

FIG. 7: BC^{2+} propagation with mean field time step 0.05 atomic units and regularization parameter 10^{-6}, for McLachlan (Eq. 46), Lagrangian (Eq. 45), and the least-norm-error simultaneous solution of the two equations in various ratios.

whereas the unconstrained calculation fails poorly, ending up with wave function error of order unity. The left panel shows that the three treatments all produce small derivative error for the duration of the pulse. However, rapid oscillations are evident. These begin immediately when using the McLachlan variational principle, as expected, because the relaxed wave function will not be stationary, but also occur with a sharp onset when using the Lagrangian principle.

For the first calculation on Be, the mean field treatment was stable without any regularization of the linear equation, Eq. (37). For the present calculation on BC^{2+}, within our mean field implementation, we have found that the Lagrangian principle generally requires regularization in order to be stable, the McLachlan principle sometimes does, and the combination generally does not. To produce Fig. 4, we have applied a regularization parameter of 10^{-6} for the McLachlan and Lagrangian calculations. This means we solve Eq.(46) or (45) using singular value decomposition, adjusting each singular value by $s_i \rightarrow \max(10^{-6}s_1, s_i)$ before inverting it, where s_1 is the greatest singular value.

In Fig. 5 the occupation number of the least occupied natural orbital is plotted. The three methods produce a result indistinguishable from the full configuration interaction result, whereas that from the unconstrained calculation is considerably different.

We now turn to the question of the performance of the methods, using typical mean field time steps. Whereas Fig. 4 was converged with a mean field time step of 0.001 atomic units, desirable time steps lie in the range of 0.01-0.05 atomic units. In Fig. 6 we show the results with a time step of 0.01. This shows what we observe to be typical behavior. The Lagrangian variational principle is unstable without significant regularization, and even with a regularization parameter of 10^{-6} shows the beginning of an instability at the end of the pulse. The McLachlan principle is unstable for realistic time steps, even with regularization. Its instability is a phase instability, apparent in the norm of the error of the wave function, but not the Hilbert space angle, in Fig. 6.

In Fig. 7 we show the results for the ad hoc combination, the least-norm-error simultaneous solution of Eqs. (46) and (45), in various ratios, with a time step of 0.05 atomic units and regularization parameter of 10^{-6}. One can see that the combination of McLachlan and Lagrange in a 1:10 ratio performs the best. When stable, the Lagrangian performs well, but is often unstable and inconsistent; the McLachlan exhibits the phase instability, which cannot be removed through regularization for large time steps. The 1:10 method is mostly the Lagrangian, with enough McLachlan to stabilize it. We have not investigated further elaborations of this ad hoc method; in particular, we have not attempted to improve it by multiplying the rows of Eqs. (46) and (45) by different factors.

VI. SUMMARY AND CONCLUSION

The MCTDHF method provides, at present, the most numerically tractable framework for accurately calculating arbitrary many-body quantum dynamics of electrons in molecules subject to strong, high-energy, ionizing laser fields. This is the subject of current interest due to improving technology for generating ultrafast laser pulses spanning from terahertz to X-ray, and the experimental possibilities that these developments create [58–61].

MCTDHF is the generalization of time-dependent configuration interaction in which the orbitals comprising the Slater determinants are time-dependent. It therefore can be described as an "adaptive" method in which the underlying basis changes to best represent the solution of the differential equation, as dictated by the chosen variational principle.

Broadly speaking, there are four barriers that have prevented the application of MCTDHF to very large polyatomic molecules, with perhaps hundreds of electrons, subject to very strong laser fields.

First, the system of nonlinear equations must first be decoupled via a numerically stable mean field approximation, making the propagation of orbitals and configuration coefficients independent over a mean field time step, as in the method of Ref. [17], which followed that of Ref. [62].

The second barrier is to further decouple the orbitals from one another. Some decoupling approximation must be applied to the orbital equation, Eq. (8), to enable improved parallelization. A viable method might involve relaxing the constraint that the orbitals be orthonormal, or the application of master and slave variational principles, or different constraints for different classes of orbitals possibly in a hierarchical fashion. However, this second barrier is a topic for future study.

The third barrier relates to multiple ionization and breakup problems and as such is less general. For a multiply ionized system, a compact spatial representation of the system using exterior complex scaling to absorb ionized electrons requires coupled N-, $(N-1)$-, etc. electron representations, such that the residual cations may be followed after ionization, if required. The dipole response in a molecule undergoing total ionization is an example of an observable whose calculation would require such a treatment. A method involving coupled density matrices has been described in Ref. [63], but awaits implementation within a full dimensional code.

The fourth barrier, that which has been addressed in the present work, is the reduction in size of the vector of configuration coefficients via N-electron representations more flexible than full configuration interaction. It is important to have overcome this barrier, even for the study of atoms and small molecules. Even for small systems, many orbitals are required to describe multiple ionization, or ionization into multiple channels, for instance, calling for restricted spaces such as configuration interaction with single and double excitations (CISD). Compact, flexible representations such as coupled cluster or matrix product states involve much more complicated restrictions on orbital occupancy, relative to the simple restricted active space (RAS) ansatz [34] described in the introduction. For a general restricted space, the allowed occupancy of one spin orbital is not independent of the occupancy of the other spin orbitals.

The MCTDHF method, however, provides considerable flexibility that has not been explored, and it is possible that one or more of these barriers may be circumvented by more creative zeroth-order ansatzes for the wave function representation, for instance, ones in which it is comprised of orbitals with compact support describing a wave function with discontinuities kept within tolerances by artificial penalty terms in the Hamiltonian [64].

Arguably, if there is one set of MCTDHF equations, it is those that result from the application of the Lagrangian variational principle [45, 47, 49] to the MCTDHF wave function ansatz. We have derived Eq. (45), which when combined with Eqs. (8) and (13), comprise the final set of MCTDHF working equations for arbitrary configuration spaces. We have also presented alternatives to Eq. (45), which result from the McLachlan variational principle and density matrix ansatzes, Eqs. (46) and (53), respectively. The conditions under which Eqs. (46) and (45) are different – under which the Dirac-Frenkel variational principle, their union, is a contradiction – have been specified for the first time. In particular, for configuration interaction, we see that if there are multiple shells that cannot be cardinally ordered, the principles must be inequivalent; they will be inequivalent for any interacting fragment description such as that used here for BC^{2+}.

All of the methods described have been shown to be capable of producing a close approximation to the full configuration interaction MCTDHF wave function and the observables calculated from it. The naive method in which the equations appropriate for full configuration interaction are used has been shown to produce substantial error that may depend strongly on the initial state.

For general restricted spaces for which the McLachlan and Lagrangian variational principles are inequivalent, we observe that the Lagrangian variational principle produces remarkable agreement with the full configuration interaction result in some measures, but that the McLachlan also performs well. By weighting the McLachlan and Lagrangian principles in a 1:10 ratio within the ad hoc combination treatment, we obtain stable propagation using a mean field time step large enough for efficient propagation within the method of Ref. [17].

These methods will permit the study of larger molecules and the use of larger numbers of orbitals for small molecules. The configuration spaces studied for Be and BC^{2+} were small, since it was our interest to perform calculations in which the effect of truncation of the Hilbert space would be severe. Converging the present calculations with respect to number of orbitals would have made the test of the method less demanding. It is important to note that the implementation of the working equation, Eq. (46), (45) or (53), requires only indexing excluded configurations that are connected to the included space via single excitations. For example, with a configuration interaction with single excitations (CIS) wave function, we must store a configuration interaction with single and double excitations (CISD) configuration list; for complete active space (CAS), we must store a list of configurations with one hole in the doubly occupied space; et cetera.

It is also important to realize that these equations, Eq. (45), (46), or (53), may be directly applied to N-electron treatments more sophisticated than configuration interaction, such as coupled cluster or matrix product states – or, N-electron treatments involving more specially designed one-electron "orbital" spaces. Ansatzes such as coupled cluster or matrix product states are powerful tools of many-body theory, and MCTDHF has already been applied to the coupled cluster representation [50–52]. However, as discussed in the introduction, that work made use of a "bivariational" principle, considering $\langle\Psi|$ and $|\Psi\rangle$ to be linearly independent. Such a treatment may ultimately prove superior to the present one, and has already shown its utility. It seems that the present equations are applicable to any Slater determinant representation, that Eq.(45) is the unique correct expression for the rates and phases of rotation of the orbitals into one another, the matrix g, regardless of the manner in which the full configuration interaction Hilbert space is contracted, within the MCTDHF wave function ansatz, satisfying the Lagrangian variational principle.

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