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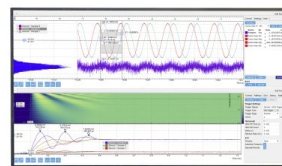
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Ab initio quantum dynamics using coupled-cluster

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The curse of dimensionality (COD) limits the current state-of-the-art *ab initio* propagation methods for non-relativistic quantum mechanics to relatively few particles. For stationary structure calculations, the coupled-cluster (CC) method overcomes the COD in the sense that the method scales polynomially with the number of particles while still being size-consistent and extensive. We generalize the CC method to the time domain while allowing the single-particle functions to vary in an adaptive fashion as well, thereby creating a highly flexible, polynomially scaling approximation to the time-dependent Schrödinger equation. The method inherits size-consistency and extensivity from the CC method. The method is dubbed orbital-adaptive time-dependent coupled-cluster, and is a hierarchy of approximations to the now standard multi-configurational time-dependent Hartree method for fermions. A numerical experiment is also given. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4718427>]

I. INTRODUCTION

Presently, the most advanced *ab initio* approximations to the time-dependent Schrödinger equation for a system of identical particles are the multi-configurational time-dependent Hartree methods for fermions (MCTDHF) and variants.^{1–4} These methods apply the time-dependent variational principle^{5–7} to an N -body wavefunction ansatz being a Slater determinant expansion using a finite (incomplete) set of $L \geq N$ orbitals φ_p with creation operators c_p^\dagger (with $\{c_p, c_q^\dagger\} = \delta_{pq}$ for fermions),

$$|\Psi_{\text{MCTDHF}}\rangle \equiv \sum_{p_1} \sum_{p_2 > p_1} \cdots \sum_{p_N > p_{N-1}} A_{p_1 \cdots p_N} c_{p_1}^\dagger c_{p_2}^\dagger \cdots c_{p_N}^\dagger |-\rangle,$$

where both the amplitudes $A_{p_1 \cdots p_N}$ and the orbitals φ_p are free to vary in single-particle space. Varying the orbitals in this way is especially important if studies of unbound systems are desired, such as the study of ionization of atoms or molecules under time-dependent external fields. The key point is that, if the orbitals are not optimized, a system in the continuum would need a *huge* fixed basis. Moreover, the *variational* determination of the orbitals compresses the wavefunction in a quasi-optimal way: from time t to $t + dt$, the basis is changed as so to minimize the L^2 norm error of the wavefunction.⁷

While powerful, MCTDHF still suffers from exponential scaling of computational complexity with respect to the number of particles N present; the “curse of dimensionality” (COD). The effect of the variational determination of the single-particle functions can be said to be a postponing of the COD to higher particle numbers. For example, for the simple TDHF, i.e., MCTDHF using precisely $L = N$ orbitals and therefore only a *single* determinant $|\phi\rangle$, qualitatively good results may be achieved, even if the system is unbound.⁸

One may attempt at reducing the exponential scaling by truncating the Slater determinant expansion at, say, single and double excitations relative to one of the determinants $|\phi\rangle = c_1^\dagger \cdots c_N^\dagger |-\rangle$, considered as a “reference determinant,”

$$|\Psi_{\text{SD}}\rangle = \left(1 + \sum_{ia} A_i^a c_a^\dagger c_i |\phi\rangle + \frac{1}{2!} \sum_{ijab} A_{ij}^{ab} c_a^\dagger c_b^\dagger c_i c_j |\phi\rangle \right) |\phi\rangle, \quad (1)$$

hoping that the higher-order excited determinants’ contribution can be neglected. (We have arbitrarily chosen intermediate normalization $\langle \phi | \Psi \rangle = 1$. In the sums, $i, j \leq N$ and $a, b > N$ is assumed.) This would achieve polynomial scaling but would destroy the important property of size-consistency:^{9,10} approximation of non-interacting subsystems separately at the singles and doubles level would not be consistent with approximating the whole at the same level; *independent* excitations of the subsystems are neglected, giving rise to artificial correlation effects.

In this article, we develop a time-dependent version of the popular coupled-cluster (CC) method for fermions, where we allow the orbitals to vary in a similar fashion to MCTDHF. We call the method *orbital adaptive time-dependent coupled-cluster* (OATDCC). Formally, the two methods are very similar, with closely related equations of motion. The main difference is the fact that coupled-cluster is not variational in the usual sense, rather, it is naturally cast in a *bivariational* setting, a generalization of the variational approach.¹¹ Bivariational functionals are *complex analytic*, while the standard variational functionals are manifestly real. Moreover, approximations of *both* the wavefunction $|\Psi\rangle$ and the complex conjugate $\langle \Psi |$ must be introduced. For the version of CC that has now become standard (referred to as “standard CC” in this article), the wavefunctions in the singles and doubles approximation (CCSD) are parametrized

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according to

$$|\Psi_{\text{CC}}\rangle \equiv e^T |\phi\rangle,$$

$$T = \sum_{ai} \tau_i^a c_a^\dagger \tilde{c}_i + \frac{1}{2!} \sum_{ijab} \tau_{ij}^{ab} c_a^\dagger c_b^\dagger \tilde{c}_i \tilde{c}_j + \dots, \quad (2a)$$

$$\langle \tilde{\Psi}_{\text{CC}} | \equiv \langle \tilde{\phi} | (1 + \Lambda) e^{-T},$$

$$\Lambda = \sum_{ai} \lambda_a^i c_i^\dagger \tilde{c}_a + \frac{1}{2!} \sum_{ijab} \lambda_{ab}^{ij} c_i^\dagger c_j^\dagger \tilde{c}_a \tilde{c}_b + \dots, \quad (2b)$$

where $\langle \tilde{\Psi}_{\text{CC}} |$ approximates $\langle \Psi | / \langle \Psi | \Psi \rangle$. The cluster operator T produces excitations with respect to a reference Slater determinant $|\phi\rangle$. The amplitudes τ_i^a and τ_{ij}^{ab} correspond (to first order) to the expansion coefficients A_i^a and A_{ij}^{ab} of Eq. (1), while the exponential form ensures size-consistency. The cluster operator Λ is a de-excitation operator, and its amplitudes λ_a^i and λ_{ab}^{ij} are essentially the parameters of $\langle \tilde{\Psi}_{\text{CC}} |$, which is composed of excitations relative to a reference bra determinant $\langle \tilde{\phi} |$. To anticipate the developments in Sec. III, we have introduced creation and annihilation operators with respect to *biorthogonal orbitals* φ_p and $\tilde{\varphi}_q$, i.e.,

$$\{\tilde{c}_p, c_q^\dagger\} = \tilde{c}_p c_q^\dagger + c_q^\dagger \tilde{c}_p \equiv \langle \tilde{\varphi}_p | \varphi_q \rangle,$$

that is to say $|\Psi\rangle$ is built using the φ_p , while $\langle \tilde{\Psi} |$ is built using $\tilde{\varphi}_p$. This relaxation of orthonormality of the orbitals is necessary to ensure that the bivariational functional is complex analytic, as discussed in Sec. II B.

It turns out the relaxation of the orbitals makes the singles amplitudes τ_i^a and λ_a^i redundant. This is analogous to the well-known fact from standard CC theory. Truncation of the remaining terms at doubles, triples, etc, then gives a hierarchy of approximations with TDHF at one end ($T = \Lambda = 0$), and full MCTDHF (no truncation of T or Λ) at the other. In between we have the doubles approximation (OATDCCD), doubles-and-triples approximation (OATDCCDT), and so on. Considering the success of the CC method for structure calculations and the MCTDHF method for dynamics, OATDCC should be a viable size-consistent alternative to MCTDHF with asymptotically much lower cost with respect to N .

Our treatment can be viewed as a generalization of the standard CC Lagrangian approach to linear response theory,^{11–15} where the Λ amplitudes are time-dependent Lagrangian multipliers as introduced in a constrained minimization of the CC energy. However, we emphasize the bivariational point of view, where Λ becomes a part of the wavefunction parametrization.

Many systems of interest are described by an explicitly time-dependent Hamiltonian, such as an atom coupled to an external electromagnetic field. Even though a time-independent Hamiltonian is assumed throughout the article, the formalism may equally well be applied to time-dependent systems without modifications.

For an excellent introduction to CC theory, see the article by Crawford,¹⁶ and the review by Bartlett and Musiał,¹⁷ as well as the textbooks by Shavitt and Bartlett¹⁰ and by Harris *et al.*¹⁸ For the present work, the article by Arponen¹¹ is fundamental, as it casts the CC theory in the bivariational frame-

work, an approach not emphasized in most introductions to CC theory.

There are few applications of CC methods to *ab initio* dynamics in the literature. It was, however, proposed as early as 1978 by Schönhammer and Gunnarsson,¹⁹ and independently by Hoodbhoy and Negele,^{20,21} who even considered time-dependent orbitals, albeit with an *explicit* time-dependence. We shall discuss their approach briefly in Sec. IV A. Recently, the standard CC ansatz using a fixed basis was applied to laser-driven dynamics of some small molecules,²² but with expectation values calculated in a different way from the usual CC approach.

In this article, a basic knowledge of CC theory as well as variational calculus is assumed. However, since the bivariational formulation of CC is not that well known, we present an overview in Sec. II. Section III is devoted to the development of the OATDCC method, but detailed mathematical derivations are deferred to the Appendixes. These are available in the supplementary material.²⁴ In Sec. IV, we further discuss and compare with MCTDHF theory. A numerical experiment on a one-dimensional model is performed in Sec. V.

The CC calculations invariably involve a lot of algebra. Therefore, in the Appendix, algebraic expressions for various quantities appearing in the OATDCCD method are listed. These are generated using symbolic algebra software developed with the SYMPY library for the programming language PYTHON.²³

In the supplementary material,²⁴ an independent derivation of MCTDHF using the bivariational principle is also given in order to shed further light on the connections between the variational and the bivariational principles. It may also serve as a helpful device for the readers in the audience not familiar with MCTDHF theory.

No attempt is made to be mathematically rigorous in this article, as like the standard CC method^{25–27} and the MCTDHF method^{7,28–30} such an analysis is expected to be quite involved. Instead, we make formal computations as if all operators present were bounded or the spaces finite dimensional.

II. BIVARIATIONAL PRINCIPLES

A. Functionals

Let A be an operator over Hilbert space \mathcal{H} , and consider the functional

$$\mathcal{E}_A : \mathcal{H}' \times \mathcal{H} \rightarrow \mathbb{C}, \quad \mathcal{E}_A[|\Psi'\rangle, |\Psi\rangle] \equiv \frac{\langle \Psi' | A | \Psi \rangle}{\langle \Psi' | \Psi \rangle}$$

defined whenever the expression makes sense. Note that the arguments are *two independent* Hilbert space elements. The functional \mathcal{E}_A is a generalization of the expectation value functional to operators that are not necessarily Hermitian, and for obvious reasons it may be called *the bivariational expectation value functional*.^{11,31} Consider the conditions for vanishing first variation, $\delta \mathcal{E}_A = 0$, for all independent variations of $\langle \Psi' |$ and $|\Psi\rangle$. A straightforward formal calculation gives the stationary conditions

$$(A - a)|\Psi\rangle = 0 \quad \text{and} \quad \langle \Psi' | (A - a) = 0, \quad (3)$$

with

$$a = \mathcal{E}_A[\langle \Psi' |, |\Psi \rangle]$$

being the value of \mathcal{E}_A at the critical point. In other words, $\langle \Psi' |$ and $|\Psi \rangle$ with $\langle \Psi' | \Psi \rangle \neq 0$ are left- and right eigenvectors, respectively, of the operator A , with eigenvalue a . Computing the eigenvalues and eigenvectors from $\delta \mathcal{E}_A = 0$ is therefore referred to as “the bivariational principle.”

Since the system Hamiltonian $H = H^\dagger$ is the generator for the time evolution of the system, we consider the following bivariational generalization of the usual action functional:^{6,11}

$$\begin{aligned} \mathcal{S}[\langle \Psi' |, |\Psi \rangle] &\equiv \int_0^T \frac{\langle \Psi'(t) | (i\hbar \frac{\partial}{\partial t} - H) | \Psi(t) \rangle}{\langle \Psi'(t) | \Psi(t) \rangle} dt \\ &= \int_0^T i\hbar \frac{\langle \Psi'(t) | \frac{\partial}{\partial t} \Psi(t) \rangle}{\langle \Psi'(t) | \Psi(t) \rangle} - \mathcal{E}_H[\langle \Psi'(t) |, |\Psi(t) \rangle] dt, \end{aligned} \quad (4)$$

where it is understood that the functional depends on the whole history of the system from time $t = 0$ to $t = T$. Suppose \mathcal{S} is stationary ($\delta \mathcal{S} = 0$) under all variations of $\langle \Psi' |$ and $|\Psi \rangle$ vanishing at the endpoints $t = 0$ and $t = T$. Straightforward manipulations now give, up to irrelevant time-dependent phase constants,

$$i\hbar \frac{\partial}{\partial t} |\Psi(t) \rangle = H |\Psi(t) \rangle \quad \text{and} \quad -i\hbar \frac{\partial}{\partial t} \langle \Psi'(t) | = \langle \Psi'(t) | H. \quad (5)$$

Consequently, the time-dependent Schrödinger equation and its complex conjugate arise from a *time-dependent bivariational principle*.

For simplicity, we have assumed that H is independent of time. It is easy to see that an explicit time-dependence $H(t)$ may be included without modifying the bivariational principle.

In both the stationary and time-dependent cases, it is convenient to do a reparametrization $\langle \tilde{\Psi} | = \langle \Psi' | \Psi \rangle^{-1} \langle \Psi' |$ so that

$$\langle \tilde{\Psi} | \Psi \rangle = 1, \quad (6)$$

eliminating the denominator in each functional. For the stationary case, this effectively eliminates one of the two eigenvalue equations (3), and makes $\langle \tilde{\Psi} |$ a unique function of $|\Psi \rangle$ and vice versa. To see this, note that since (a) eigenvectors corresponding to different eigenvalues are *always* orthogonal, and since (b) $\langle \tilde{\Psi} | \Psi \rangle = 1$, $\langle \tilde{\Psi} |$ is uniquely given by $|\Psi \rangle$ at the critical point as the biorthogonal left eigenvector corresponding to the right eigenvector $|\Psi \rangle$. For the time-dependent case, the normalization $\langle \tilde{\Psi}(t) | \Psi(t) \rangle = 1$ eliminates one of the Schrödinger equations (5), but the phase ambiguity is still present for the remaining equation, a similar situation as the stationary case.

Unless otherwise stated, the normalization (6) is assumed in the following, and it is indicated by the tilde $\langle \tilde{\Psi} |$ instead of the prime $\langle \Psi' |$.

It is also natural to assume some secondary normalization on $|\Psi \rangle$, such that the critical point actually becomes locally unique for both the time-dependent and time-independent cases. (“Locally unique” means that there may be many critical points but that they are isolated.) This is done in

CC theory using intermediate normalization. This removes norm and phase ambiguity in both time-dependent and time-independent pictures.

B. Generating approximations from submanifolds

Contrary to the usual variational principles, in the bivariational principles *the wavefunction and its complex conjugate are formally independent*. When applied to Hermitian operators this opens up possibilities for more general approximations of spectra and dynamics compared to the standard variational principles. However, where the usual “Hermitian” time-dependent variational principle is, to paraphrase Kramer and Saraceno,⁶ a deaf and dumb procedure that always gives an answer, the bivariational principle requires a more careful approach, as we will discuss in this section.

The bivariational principles are little known, perhaps because one must be more careful with them. The author has found only a few relevant sources in the literature apart from Arponen’s seminal coupled-cluster article,¹¹ the most relevant ones being a brief mention by Killingbeck in his review on perturbation theory³² and a discussion by Löwdin *et al.*³¹ concerning self-consistent field-calculations on non-Hermitian (complex scaled) Hamiltonians. The bivariational principle seems largely unexplored.

It is important to note that the standard critique of coupled-cluster is that it is “non-variational”. While it is true that it makes estimation of errors harder, it is not a serious drawback in any other sense, since the calculation is firmly rooted in a variational principle. For example, if H does not depend explicitly on time, $(d/dt)\mathcal{E}_H \equiv 0$, i.e., energy is conserved. Probability is always conserved, $(d/dt)\mathcal{E}_1 = (d/dt)\langle \tilde{\Psi} | \Psi \rangle \equiv 0$. Just like the usual time-dependent variational principle, these are simple consequences of the symmetries of the action functional.

For bivariational approximations, one introduces different parametrizations of the wavefunction $|\Psi \rangle$ and its complex conjugate $\langle \tilde{\Psi} |$, which is contrary to the usual variational principle. Notice that in Eq. (2), different parametrizations $|\Psi_{\text{CC}} \rangle$ and $\langle \tilde{\Psi}_{\text{CC}} |$ are used, but $\langle \tilde{\Psi}_{\text{CC}} | \Psi_{\text{CC}} \rangle = 1$. Formally, we do a variation over a manifold $\mathcal{M} \subset \mathcal{H}' \times \mathcal{H}$, i.e., $(\langle \tilde{\Psi} |, |\Psi \rangle) \in \mathcal{M}$. Alternatively, one may think of \mathcal{M} as a subset of rank-one density operators $u = |\tilde{\Psi} \rangle \langle \Psi |$, $\text{Tr}(u) = 1$, where $u^\dagger \neq u$ is allowed.

As \mathcal{H} is a complex space, the functionals \mathcal{E}_H and \mathcal{S} are complex. On the other hand, in the usual variational principle, the functionals are always real-valued. This has some interesting consequences. We now briefly discuss four important aspects: the analytic structure of the functionals, the need for systematic refinability of \mathcal{M} , interpretations of complex critical points, and even-dimensionality of \mathcal{M} .

The parametrization of $u = (\langle \tilde{\Psi} |, |\Psi \rangle)$ must be complex analytic, at least locally. A parametrization which is *not* analytic is, in essence, a real parametrization, since it depends on both the real and imaginary parts of the (local) coordinates $z \in \mathbb{C}^n$ separately, and not only $\text{Re } z + i \text{Im } z$. Thus, we have $2n$ real coordinates. Since *both* $\text{Re } \delta \mathcal{S}$ and $\text{Im } \delta \mathcal{S}$ must vanish, this leads to $4n$ equations. Unless there is some extra

structure, i.e., that $\text{Im } \mathcal{S} \equiv 0$ such as in the standard variational principle, a solution cannot be expected to exist. Correspondingly, the bivariational functionals should be complex analytic. Nowhere should explicitly real parameters occur, and nowhere should parameters be explicitly complex conjugated.

Suppose the system Hamiltonian H is bounded from below, i.e., the variational expectation value is bounded from below. This is the source of the usefulness of the Hermitian stationary variational principle, since *any* parametrization gives an upper bound for the ground state energy. A potential danger with the bivariational expectation value functional is that it is *not* bounded from below, even if H is. Indeed, \mathcal{E}_H is complex analytic and can take on values in the whole of \mathbb{C} . One cannot insert “just anything” and hope to get sensible results by computing critical points. To avoid this problem, and to allow for the computation of error estimates, \mathcal{M} should be chosen in a way that is in some sense systematically refinable towards the full space $\mathcal{H}' \times \mathcal{H}$, e.g., there is some discretization parameter that can be used to measure the accuracy. In CC theory, this parameter is the truncation level of the cluster operators and the number L of orbitals used.

Critical values of \mathcal{E}_H for $H = H^\dagger$ may be complex, even though the exact eigenvalues are always real. However, if $H = H^\dagger$, the imaginary values of the critical values generally “should be small” if \mathcal{M} is chosen “well enough,” and may correspondingly be ignored in order to assign a physical interpretation to the critical value, i.e., energy. This is also justified by the fact that the functional $\text{Re } \mathcal{E}_H$ has the same critical points as \mathcal{E}_H if the parametrization is analytic.

For the approximate manifold \mathcal{M} , we must be certain that the critical point $(\langle \tilde{\Psi} |, |\Psi \rangle)$ is locally unique. In particular, this is necessary for the corresponding critical *value*, i.e., $\mathcal{E}_A[\langle \tilde{\Psi} |, |\Psi \rangle]$, to be unique for any observable A . Otherwise, the physical state cannot be said to be well defined. Intuitively, the parameters must then come in pairs; roughly stated every parameter in $|\Psi \rangle$ should have a parameter in $\langle \tilde{\Psi} |$.

This can be shown explicitly. Suppose $\langle \tilde{\Psi} |$ and $|\Psi \rangle$ are parametrized locally using some set of complex variables $z(t) \in \mathbb{C}^n$, i.e., we have an approximating manifold $\mathcal{M} \subset \mathcal{H}' \times \mathcal{H}$ whose dimension is assumed to be finite for simplicity. The energy expectation functional becomes $E[z] = \mathcal{E}[\langle \tilde{\Psi}(z) |, |\Psi(z) \rangle]$, and the time-dependent bivariational functional becomes

$$F[z(\cdot)] = \int_0^T i\hbar \sum_k \langle \tilde{\Psi}(z) | \frac{\partial \Psi}{\partial z_k}(z) \dot{z}_k - E[z] dt. \quad (7)$$

The first variation becomes

$$\delta F[z, \delta z] = \int_0^T \sum_{kl} \delta z_l \left(i\hbar C_{lk} \dot{z}_k - \frac{\partial E}{\partial z_l} \right) dt, \quad (8)$$

where the complex anti-symmetric matrix $C(z)$ is given by

$$C(z)_{jk} = \left\langle \frac{\partial \tilde{\Psi}}{\partial z_j} \middle| \frac{\partial \Psi}{\partial z_k} \right\rangle - \left\langle \frac{\partial \tilde{\Psi}}{\partial z_k} \middle| \frac{\partial \Psi}{\partial z_j} \right\rangle. \quad (9)$$

The stationary point is therefore given by solutions of the differential equation

$$i\hbar C(z) \dot{z} = \nabla_z E(z). \quad (10)$$

For any anti-symmetric matrix, if λ is an eigenvalue of multiplicity m , so is $-\lambda$, implying that $C(z)$ is not invertible if n is odd, since it must have a zero eigenvalue. Consequently, the approximation manifold must be complex even dimensional if Eq. (10) is to have a unique solution.

III. THE OATDCC METHOD

A. Biorthogonality of orbitals

The fact that we require our bivariational functionals to be analytic is important, as it necessitates the relaxation of the orthonormality of the orbitals φ_p by introducing a second set of biorthogonal orbitals $\tilde{\varphi}_q$, being in effect *approximate* complex conjugates of each other. However, they are introduced as *independent* complex parameters.

Consider a subspace $\mathcal{V} \subset \mathcal{H}$, generated by a finite set of orbitals $\Phi = (\varphi_1, \varphi_2, \dots, \varphi_L)$, which we write $\mathcal{V} = \mathcal{V}[\Phi]$. (We interpret φ_p as the p th column of the matrix Φ .) These orbitals need not be orthonormal; it is only the one-body space spanned by the φ_p that matters. In the bivariational functionals, we desire to vary $\langle \tilde{\Psi} |$ in as large space $\tilde{\mathcal{V}} \subset \mathcal{H}'$ as possible, while guaranteeing the existence of a dual vector non-orthogonal to $|\Psi \rangle \in \mathcal{V}$. (Otherwise, the denominator in Eq. (4) may vanish.) The only restriction on the space $\tilde{\mathcal{V}}$ is that it is generated by a set of dual orbitals $\tilde{\Phi} = (\tilde{\varphi}_1; \dots; \tilde{\varphi}_L)$ (where we interpret $\tilde{\varphi}_p$ as the p th row of $\tilde{\Phi}$). Sometimes we will stress the fact that φ_p and $\tilde{\varphi}_p$ are single-particle ket and bra-functions, respectively, by explicitly writing $|\varphi_p \rangle$ and $\langle \tilde{\varphi}_p |$.

Consider the overlap matrix S with matrix elements $S_{pq} = \langle \tilde{\varphi}_p | \varphi_q \rangle$. Since the spaces $\mathcal{V}[\Phi]$ and $\tilde{\mathcal{V}}[\tilde{\Phi}]$ only depend on the subspaces spanned by Φ and $\tilde{\Phi}$, respectively, we may via a suitable transform assume that S is diagonal with only 1s and 0s on the diagonal. If S is invertible, then the orbitals are biorthogonal,

$$\langle \tilde{\varphi}_p | \varphi_q \rangle = \delta_{pq}.$$

It is straightforward to show the following claim: the existence of a $\langle \tilde{\Psi} | \in \tilde{\mathcal{V}}[\tilde{\Phi}]$ for every $|\Psi \rangle \in \mathcal{V}[\Phi]$ such that $\langle \tilde{\Psi} | \Psi \rangle \neq 0$ is equivalent to requiring the overlap matrix $S_{pq} = \langle \tilde{\varphi}_p | \varphi_q \rangle$ to be invertible, i.e., that the orbitals are biorthogonal. (A corresponding claim where the roles of $|\Psi \rangle$ and $\langle \tilde{\Psi} |$ are reversed is equivalent.)

Biorthogonality is equivalent to

$$\langle \tilde{\varphi}_{p_1 \dots p_N} | \varphi_{q_1, \dots, q_N} \rangle = \delta_{p_1, q_1} \dots \delta_{p_N, q_N}$$

for the Slater determinant bases of $\tilde{\mathcal{V}}$ and \mathcal{V} , given by

$$|\phi_{p_1 \dots p_N} \rangle \equiv c_{p_1}^\dagger c_{p_2}^\dagger \dots c_{p_N}^\dagger | - \rangle \quad \text{and}$$

$$\langle \tilde{\phi}_{q_1 \dots q_N} | \equiv \langle - | \tilde{c}_{q_N} \tilde{c}_{q_{N-1}} \dots \tilde{c}_{q_1},$$

respectively. (We assume $p_1 < p_2 < \dots$ and $q_1 < q_2 < \dots$.)

To prove the claim, let p be given. Suppose that there is a p' such that $\langle \tilde{\varphi}_{p'} | \varphi_p \rangle = 0$. Then, if $|\Psi \rangle = |\phi_{p', p_2, \dots, p_N} \rangle$, no $\langle \tilde{\Psi}' | \in \tilde{\mathcal{V}}$ is non-orthogonal to $|\Psi \rangle$. Conversely, suppose that no such p' exists. Then, given an arbitrary $0 \neq |\Psi \rangle \in \mathcal{V}$, $\langle \tilde{\phi}_{p_1, \dots, p_N} | \Psi \rangle$ must be nonzero for some p_1, \dots, p_N . This proves the claim.

The creation operators are expanded using field creation and annihilation operators as

$$c_p^\dagger \equiv \int \varphi_p(x) \psi(x)^\dagger dx \quad (11a)$$

and

$$\tilde{c}_p \equiv \int \tilde{\varphi}_p(x) \psi(x) dx, \quad (11b)$$

which may be taken as a definition. The biorthogonality condition is now equivalent to an anticommutator relation

$$\{\tilde{c}_p, c_q^\dagger\} \equiv \tilde{c}_p c_q^\dagger + c_q^\dagger \tilde{c}_p \equiv \langle \tilde{\varphi}_p | \varphi_q \rangle = \delta_{pq}, \quad (12)$$

proven by inserting Eqs. (11a) and (11b). Thus, Wick's theorem^{10,33} holds in its usual form, simply replacing c_p with the operator \tilde{c}_p .

In standard CC theory and virtually every other many-body method, $\varphi_p(x)^* \equiv \tilde{\varphi}_p(x)$, so that $\mathcal{V} \equiv \tilde{\mathcal{V}}$. We stress that the relaxation of this requirement allows for a complex analytic functional, which is essential for the bivariational principle.

We now comment on the form of the Hamiltonian in second quantization. For simplicity, we assume that the Hamiltonian contains at most two-body forces, i.e.,

$$H = \sum_{i=1}^N h(i) + \frac{1}{2} \sum_{i,j,i \neq j}^N u(i,j), \quad (13)$$

in first quantization, where $h(i)$ is an operator acting only on the degrees of freedom for particle i , and $u(i,j)$ acts only on the degrees of freedom of the pair (i,j) . For molecular electronic systems in the Born–Oppenheimer approximation, $h(i)$ is the sum of kinetic energy and the nuclear attraction potential, while $u(i,j)$ is the Coulomb repulsion between electrons i and j .

Suppose now Π is the projection operator

$$\Pi \equiv |\phi\rangle \langle \tilde{\phi}| + \sum_{\mu} |\phi_{\mu}\rangle \langle \tilde{\phi}^{\mu}|, \quad (14)$$

which projects a dual state onto $\tilde{\mathcal{V}}[\tilde{\Phi}]$ and a state onto $\mathcal{V}[\Phi]$; the sum is over all Slater determinants. For any $|\Psi\rangle \in \mathcal{V}$, $\Pi|\Psi\rangle = |\Psi\rangle$, and for any $\langle\Psi'| \in \tilde{\mathcal{V}}$, $\langle\Psi'|\Pi = \langle\Psi'|$. However, $\Pi \neq \Pi^\dagger$ so it is not an orthogonal projector. We now have, for the CC ansatz,

$$\langle\Psi'|H|\Psi\rangle = \langle\Psi'|\Pi H \Pi|\Psi\rangle,$$

where

$$\begin{aligned} \Pi H \Pi &= \sum_{pq} \langle \tilde{\varphi}_p | h | \varphi_q \rangle c_p^\dagger \tilde{c}_q + \frac{1}{4} \sum_{pqrs} \langle \tilde{\varphi}_p \tilde{\varphi}_r | u | \varphi_q \varphi_s \rangle_{AS} c_p^\dagger c_r^\dagger \tilde{c}_s \tilde{c}_q \\ &\equiv \sum_{pq} h_{pq}^p c_p^\dagger \tilde{c}_q + \frac{1}{4} \sum_{pqrs} u_{qs}^{pr} c_p^\dagger c_r^\dagger \tilde{c}_s \tilde{c}_q. \end{aligned} \quad (15)$$

The two-body integrals are anti-symmetrized according to the standard in CC theory and are given by

$$\langle \tilde{\varphi}_p \tilde{\varphi}_r | u | \varphi_q \varphi_s \rangle_{AS} \equiv \langle \tilde{\varphi}_p \tilde{\varphi}_r | u | \varphi_q \varphi_s \rangle - \langle \tilde{\varphi}_p \tilde{\varphi}_r | u | \varphi_s \varphi_q \rangle, \quad (16a)$$

$$\langle \tilde{\varphi}_p \tilde{\varphi}_r | u | \varphi_q \varphi_s \rangle \equiv \int \tilde{\varphi}_p(x) \tilde{\varphi}_r(y) u(x,y) \varphi_q(x) \varphi_s(y) dx dy. \quad (16b)$$

The reason for introducing the operator Π is this: The Hamiltonian is *defined* by its expression (13), and not by Eq. (15). This definition does not depend on any part of the parametrization, in particular, it is independent of the orbitals. However, when *evaluating* expressions involving the Hamiltonian, such as the expectation value, the projected operator $\Pi H \Pi$ is easier and equivalent: Wick's theorem can be applied. It is important to note, that unless the orbitals are complete, $\Pi H \Pi \neq H$.

B. The coupled-cluster ansatz

As usual in CC theory, the orbitals are divided into occupied (the N first) and virtual orbitals (the $L - N$ last). By common convention, indices i, j, k , etc., denote occupied orbitals, while indices a, b, c , etc., denote virtual orbitals.

The CC parametrization of arbitrary wavefunctions in $\mathcal{V}[\Phi]$ and $\tilde{\mathcal{V}}[\Phi]$ is given by

$$|\Psi\rangle = e^T |\phi\rangle \quad \text{and} \quad \langle\Psi'| = \langle\tilde{\phi}| e^{T'}, \quad (17)$$

where $|\phi\rangle$ and $\langle\tilde{\phi}|$ are the reference determinants

$$|\phi\rangle = c_1^\dagger c_2^\dagger \cdots c_N^\dagger |-\rangle, \quad \langle\tilde{\phi}| = \langle - | \tilde{c}_N \tilde{c}_{N-1} \cdots \tilde{c}_1. \quad (18)$$

Here, T is an excitation operator on the form

$$T = \sum_{\mu} \tau^{\mu} X_{\mu} = \sum_{ai} \tau_i^a c_a^\dagger \tilde{c}_i + \frac{1}{2!} \sum_{abij} \tau_{ij}^{ab} c_a^\dagger c_b^\dagger \tilde{c}_i \tilde{c}_j + \cdots \quad (19)$$

and T' is a de-excitation operator on the form

$$T' = \sum_{\mu} \tau'_{\mu} \tilde{X}^{\mu} = \sum_{ai} (\tau')_{ai}^i \tilde{c}_a + \frac{1}{2!} \sum_{abij} (\tau')_{ab}^{ij} \tilde{c}_i \tilde{c}_j c_a^\dagger c_b^\dagger + \cdots \quad (20)$$

We have introduced a generic index μ for short-hand summation over (linearly independent) excitations and de-excitations. Note that de-excitation operators are not simply adjoints of excitation operators, due to bi-orthogonality replacing orthonormality.

It is worthwhile to note at this point, that operators T and T' depend on *both* the amplitudes *and* the orbitals, $T = T(\tau, \tilde{\Phi}, \Phi)$, and similarly for T' . In standard CC theory, one usually thinks of the amplitudes as the primary unknown, since the orbitals are fixed, and since dependence on τ is linear and one-to-one. In the OATDCC theory, we must be careful, for example, when computing $\partial T / \partial \tau$.

We also note, that even though X_{μ} depends explicitly on the dual orbitals through the appearance of \tilde{c}_i , the function $|\phi_{\mu}\rangle \equiv X_{\mu} |\phi\rangle$ does not: \tilde{c}_i is only responsible for removing φ_i (not $\tilde{\varphi}_i$!) from a determinant. The Slater determinants $|\phi_{\mu}\rangle$ are easily seen to form a basis for \mathcal{V} together with $|\phi\rangle$, see Eq. (14).

The bivariational expectation \mathcal{E}_H now reads

$$\mathcal{E}_H[\tau', \tau, \tilde{\Phi}, \Phi] = \frac{\langle \tilde{\phi} | e^{T'} H e^T | \phi \rangle}{\langle \tilde{\phi} | e^{T'} e^T | \phi \rangle}. \quad (21)$$

Following Arponen,¹¹ we may perform a simple change of variables from the pair (T', T) to the pair (Λ, T) with Λ being a de-excitation operator, such that

$$\langle \tilde{\Psi} | = \frac{\langle \Psi' |}{\langle \Psi' | \Psi \rangle} = \langle \tilde{\phi} | (1 + \Lambda) e^{-T}. \quad (22)$$

Equation (21) becomes

$$\mathcal{E}_H[\lambda, \tau, \tilde{\Phi}, \Phi] = \langle \tilde{\phi} | (1 + \Lambda) e^{-T} H e^T | \phi \rangle. \quad (23)$$

Disregarding the dependence on $\tilde{\Phi}$ and Φ , this functional is the well-known CC expectation functional.^{11,13,14} The usual interpretation for λ_μ is as Lagrange multipliers for a constrained minimization of the energy which is equivalent to the standard CC equations.¹⁶ In our case, however, it is interpreted as part of the parametrization of the approximate dual wavefunction which enters the expectation functional. λ_μ should be treated on equal footing with τ^μ : they are equally important.

The fundamental approximation idea in CC theory is now to truncate the expansion for T and Λ . For example, for the CCSD approximation, one takes

$$T \approx T_1 + T_2 \quad \text{and} \quad \Lambda \approx \Lambda_1 + \Lambda_2,$$

neglecting amplitudes with $n > 2$. In the following discussion, the truncation level n should be considered a parameter of the ansatz.

It is well known that the evaluation of \mathcal{E} scales polynomially with the truncation level and the number of orbitals L , in contrast to full configuration-interaction (FCI) type parameterizations. This follows from the no less than remarkable fact that the Baker–Campbell–Hausdorff expansion of the similarity transform $\exp(-T)H\exp(T)$ truncates *identically* after a finite number of terms, regardless of the number of particles present. For the two-body Hamiltonian (13), four nested commutators suffice. It follows that $\mathcal{E}_H[\Lambda, T, \tilde{\Phi}, \Phi]$ is a fourth order polynomial in $\tau = (\tau^\mu)$ and linear in $\lambda = (\lambda_\mu)$. This polynomial can be evaluated using Wick's theorem, see the Appendix.

C. The OATDCC action functional

Having established the form of the OATDCC expectation functional, we now turn to the evaluation of the corresponding action-like functional \mathcal{S} defining the Schrödinger dynamics,

$$\begin{aligned} \mathcal{S}[\lambda, \tau, \tilde{\Phi}, \Phi] &= \int_0^T \langle \tilde{\phi} | (1 + \Lambda) e^{-T} \left(i\hbar \frac{\partial}{\partial t} - H \right) e^T | \phi \rangle dt \\ &= \int_0^T i\hbar \langle \tilde{\phi} | (1 + \Lambda) e^{-T} \frac{\partial}{\partial t} e^T | \phi \rangle \\ &\quad - \mathcal{E}_H[\lambda(t), \tau(t), \tilde{\Phi}(t), \Phi(t)] dt. \end{aligned} \quad (24)$$

To evaluate the explicit functional dependence on the time derivatives of τ and Φ , we must compute $\frac{\partial}{\partial t} |\Psi\rangle = \frac{\partial}{\partial t} e^T |\phi\rangle$. To this end, we use the expansion

$$|\Psi\rangle = \Pi |\Psi\rangle = |\phi\rangle + \sum_\mu A^\mu |\phi_\mu\rangle,$$

$$A^\mu = A^\mu(\tau) = \langle \tilde{\phi}^\mu | e^T | \phi \rangle,$$

where the summation is *not* truncated at any level, even if τ^μ is. Since Wick's theorem only uses the anti-commutator (12), the coefficients $A^\mu = A^\mu(\tau)$ do not depend explicitly on the orbitals, only on the (possibly truncated) amplitudes τ . Moreover, we compute the derivative of a Slater determinant via

$$\begin{aligned} \frac{\partial}{\partial t} c_{p_1}^\dagger c_{p_2}^\dagger \cdots c_{p_N}^\dagger | - \rangle &= \dot{c}_{p_1}^\dagger c_{p_2}^\dagger \cdots c_{p_N}^\dagger | - \rangle + c_{p_1}^\dagger \dot{c}_{p_2}^\dagger \cdots c_{p_N}^\dagger | - \rangle + \cdots \\ &= \left(\sum_q \dot{c}_q^\dagger \tilde{c}_q \right) c_{p_1}^\dagger c_{p_2}^\dagger \cdots c_{p_N}^\dagger | - \rangle \\ &= D c_{p_1}^\dagger c_{p_2}^\dagger \cdots c_{p_N}^\dagger | - \rangle. \end{aligned}$$

Here, we defined an operator D given by

$$D \equiv \sum_q \dot{c}_q^\dagger \tilde{c}_q. \quad (25)$$

The operator D , unlike H , depends explicitly on the orbitals. We get

$$\begin{aligned} \frac{\partial}{\partial t} |\Psi\rangle &= \sum_\mu \left(\frac{\partial}{\partial t} A^\mu(\tau) \right) |\phi_\mu\rangle + D |\phi\rangle + \sum_\mu A^\mu(\tau) D |\phi_\mu\rangle \\ &= \left(\sum_v \dot{\tau}^v \frac{\partial}{\partial \tau^v} + D \right) |\Psi\rangle = \left(\sum_v \dot{\tau}^v X_v + D \right) |\Psi\rangle. \end{aligned} \quad (26)$$

For the time-derivative part of the functional integrand, we now get

$$\begin{aligned} i\hbar \langle \tilde{\phi} | (1 + \Lambda) e^{-T} \frac{\partial}{\partial t} e^T | \phi \rangle \\ &= i\hbar \langle \tilde{\phi} | \left(1 + \sum_\mu \lambda_\mu \tilde{X}^\mu \right) e^{-T} \left(\sum_v \dot{\tau}^v X_v + D \right) e^T | \phi \rangle \\ &= i\hbar \sum_\mu \lambda_\mu \dot{\tau}^\mu + i\hbar \langle \tilde{\phi} | (1 + \Lambda) e^{-T} \Pi D \Pi e^T | \phi \rangle. \end{aligned}$$

The projected operator $\Pi D \Pi$ is given by

$$\Pi D \Pi = D_0 \equiv \sum_{pq} \langle \tilde{\phi}_p | \dot{\phi}_q \rangle c_p^\dagger \tilde{c}_q.$$

Finally, we obtain

$$\mathcal{S}[\lambda, \tau, \tilde{\Phi}, \Phi] = \int_0^T i\hbar \sum_\mu \lambda_\mu \dot{\tau}^\mu - \mathcal{E}_{H-i\hbar D_0}[\lambda, \tau, \tilde{\Phi}, \Phi] dt \quad (27a)$$

$$= \int_0^T i\hbar \lambda_\mu \dot{\tau}^\mu + \rho_p^q (h_q^p - i\hbar \eta_q^p) + \frac{1}{4} \rho_{pr}^{qs} u_{qs}^{pr} dt, \quad (27b)$$

where

$$\begin{aligned}\rho_p^q &= \rho_p^q(\lambda, \tau) \equiv \langle \tilde{\phi} | (1 + \Lambda) e^{-T} c_p^\dagger \tilde{c}_q e^T | \phi \rangle, \\ \rho_{pr}^{qs} &= \rho_{pr}^{qs}(\lambda, \tau) \equiv \langle \tilde{\phi} | (1 + \Lambda) e^{-T} c_p^\dagger c_r^\dagger \tilde{c}_s \tilde{c}_q e^T | \phi \rangle, \\ h_q^p &= h_q^p(\tilde{\Phi}, \Phi) \equiv \langle \tilde{\varphi}_p | h | \varphi_q \rangle, \\ \eta_q^p &= \eta_q^p(\tilde{\Phi}, \dot{\Phi}) \equiv \langle \tilde{\varphi}_p | \dot{\varphi}_q \rangle, \\ u_{qs}^{pr} &= u_{qs}^{pr}(\tilde{\Phi}, \Phi) \equiv \langle \tilde{\varphi}_p \tilde{\varphi}_r | u | \varphi_q \varphi_s \rangle_{\text{AS}}.\end{aligned}$$

In Eq. (27b), we introduced the Einstein summation convention over repeated indices of opposite vertical placement.

The quantities ρ_p^q and ρ_{pr}^{qs} (whose index placement should be noted) are the CC reduced one- and two-particle density matrices, respectively, and are not explicitly dependent on the orbitals since they are evaluated using Wick's theorem depending only on the fundamental anti-commutator. They therefore only depend on the amplitudes. Similarly, the one-particle integrals h_q^p , η_q^p and the two-particle integrals u_{qs}^{pr} only depend on the orbitals. These facts dramatically simplify the derivation of the stationary action conditions.

D. Equations of motion

The equations of motion for the amplitudes and orbitals arise from the principle of least action, $\delta S = 0$ for all independent variations of the parameters. A detailed derivation is quite involved and is deferred to the Appendixes in the supplementary material.²⁴

It is well known in CC theory that the singles amplitudes can be formally eliminated by a rotation among the virtual and occupied orbitals. This is also true for the OATDCC method, and for that reason λ_a^i and τ_i^a can be eliminated from the equations. Thus, it is sufficient to take $T = T_2 + T_3 + \dots$ and $\Lambda = \Lambda_2 + \Lambda_3 + \dots$, with a truncation at the desired level. The equations of motion for the amplitudes read

$$\begin{aligned}i\hbar \dot{\tau}^\mu &= \frac{\partial}{\partial \lambda_\mu} \mathcal{E}_{H-i\hbar D_0}[\lambda, \tau, \tilde{\Phi}, \Phi] \\ &= \langle \tilde{\phi}_\mu | e^{-T} (H - i\hbar D_0) e^T | \phi \rangle,\end{aligned}\quad (28a)$$

$$\begin{aligned}-i\hbar \dot{\lambda}_\mu &= \frac{\partial}{\partial \tau^\mu} \mathcal{E}_{H-i\hbar D_0}[\lambda, \tau, \tilde{\Phi}, \Phi] \\ &= \langle \phi | (1 + \Lambda) e^{-T} [H - i\hbar D_0, X_\mu] e^T | \phi \rangle.\end{aligned}\quad (28b)$$

These must hold for all μ included in the approximation. The right-hand sides are polynomials in the amplitudes and are seen to be identical to the usual right-hand sides of standard CC amplitude equations, but with a modified Hamiltonian due to the time-dependent basis.

As is well known in MCTDHF theory, a gauge condition is needed on the time derivatives of the orbitals to make these unique. In OATDCC theory, a similar consideration arises from the basic fact that rotations among the occupied and virtual orbitals *separately* can be compensated by a corresponding transformation of the amplitudes. In the Appendix, it is shown that it is correspondingly sufficient to consider orbital

time derivatives of the form

$$\begin{aligned}|\dot{\varphi}_q\rangle &= (P + Q)|\dot{\varphi}_q\rangle = \sum_p |\varphi_p\rangle \langle \tilde{\varphi}_p | \dot{\varphi}_q \rangle + Q|\dot{\varphi}_q\rangle \\ &= \sum_p \eta_q^p |\varphi_p\rangle + Q|\dot{\varphi}_q\rangle\end{aligned}\quad (29a)$$

$$\begin{aligned}\langle \dot{\tilde{\varphi}}_p | &= \langle \dot{\tilde{\varphi}}_p | (P + Q) = \sum_q \langle \dot{\tilde{\varphi}}_p | \varphi_q \rangle \langle \tilde{\varphi}_q | + \langle \dot{\tilde{\varphi}}_p | Q \\ &= - \sum_q \eta_q^p \langle \tilde{\varphi}_q | + \langle \dot{\tilde{\varphi}}_p | Q\end{aligned}\quad (29b)$$

with $\eta_j^i = \eta_b^a = 0$, $\eta_q^p = \langle \tilde{\varphi}_p | \dot{\varphi}_q \rangle = -\langle \dot{\tilde{\varphi}}_p | \varphi_q \rangle$. Here, $P = \Phi \tilde{\Phi} = \sum_p |\varphi_p\rangle \langle \tilde{\varphi}_p |$ is the projection operator onto the single-particle space defined by the orbitals, and $Q = 1 - P$ projects onto “the rest”. (In MCTDHF theory, η may be taken identically zero, but this is not possible for CC parametrizations.)

The equations of motion for the nonzero P -components η_i^a and η_a^i of the orbital derivatives read

$$\begin{aligned}i\hbar \sum_{bj} A_{aj}^{ib} \eta_b^j &= \sum_p \rho_p^i h_a^p - \sum_q \rho_a^q h_q^i \\ &+ \frac{1}{2} \left[\sum_{prs} \rho_{pr}^{is} u_{as}^{pr} - \sum_{rqs} \rho_{ar}^{qs} u_{qs}^{ir} \right],\end{aligned}\quad (30a)$$

$$\begin{aligned}-i\hbar \sum_{bj} A_{bi}^{ja} \eta_j^b &= \sum_p \rho_p^a h_i^p - \sum_q \rho_i^q h_q^a \\ &+ \frac{1}{2} \left[\sum_{prs} \rho_{pr}^{as} u_{is}^{pr} - \sum_{rqs} \rho_{ir}^{qs} u_{qs}^{ar} \right] + i\hbar \dot{\rho}_i^a.\end{aligned}\quad (30b)$$

Note the presence of $\dot{\rho}_i^a$ in the latter equation. This arises as a consequence of the asymmetric role of Λ and T in the CC parametrization. The equations are exhibited as a linear system of algebraic equations for the nonzero elements of η . The matrix elements A_{aj}^{ib} are defined by

$$A_{aj}^{ib} \equiv \langle \tilde{\Psi} | [c_j^\dagger \tilde{c}_b, c_a^\dagger \tilde{c}_i] | \Psi \rangle = \delta_a^b \rho_j^i - \delta_j^i \rho_a^b. \quad (31)$$

Finally, the Q -part of the orbital derivatives are given by

$$\begin{aligned}i\hbar \sum_q \rho_p^q Q \frac{\partial}{\partial t} |\varphi_q\rangle &= \sum_q \rho_p^q Q h |\varphi_q\rangle \\ &+ \sum_{qrs} \rho_{pr}^{qs} Q W_s^r |\varphi_q\rangle \quad \text{for all } p,\end{aligned}\quad (32a)$$

$$\begin{aligned}-i\hbar \sum_p \rho_p^q \left(\frac{\partial}{\partial t} \langle \tilde{\varphi}_p | \right) Q &= \sum_p \rho_p^q \langle \tilde{\varphi}_p | h Q \\ &+ \sum_{prs} \rho_{pr}^{qs} \langle \tilde{\varphi}_p | W_s^r Q \quad \text{for all } q.\end{aligned}\quad (32b)$$

The operators W_s^r are mean-field operators defined by

$$\begin{aligned} W_s^r |\psi\rangle &\equiv \langle \cdot | \tilde{\varphi}_r | u | \psi \varphi_s \rangle \\ &\equiv \int dx \left[\int dx' \tilde{\varphi}_r(x') u(x, x') \psi(x) \varphi_s(x') \right] |x\rangle. \end{aligned} \quad (33)$$

E. The doubles approximation: OATDCCD

The simplest non-trivial OATDCC case is the OATD-CCD approximation. The wavefunction parameters are, in addition to the orbitals $\tilde{\Phi}$ and Φ , the amplitudes $\tau = (\tau_{ij}^{ab})$ and $\lambda = (\lambda_{ab}^{ij})$. In the Appendix, a complete listing of the algebraic expressions needed to evaluate the equations of motion is given. In particular, as shown in the Appendix, the only nonzero elements of the one-body reduced density matrix become ρ_i^j and ρ_a^b , which simplifies the equations of motion. The amplitude equations read

$$\begin{aligned} i\hbar \dot{\tau}_{ij}^{ab} &= \frac{\partial}{\partial \lambda_{ab}^{ij}} \mathcal{E}_H[\lambda, \tau, \tilde{\Phi}, \Phi] = \langle \tilde{\phi}_{ij}^{ab} | e^{-T} H e^T | \phi \rangle, \quad (34a) \\ -i\hbar \dot{\lambda}_{ab}^{ij} &= \frac{\partial}{\partial \tau_{ij}^{ab}} \mathcal{E}_H[\lambda, \tau, \tilde{\Phi}, \Phi] = \langle \tilde{\phi} | (1 + \Lambda) e^{-T} [H, X_{ab}^{ij}] e^T | \phi \rangle. \end{aligned} \quad (34b)$$

The P -space orbital equations read

$$\begin{aligned} i\hbar \sum_{bj} A_{aj}^{ib} \eta_j^i &= \sum_j \rho_j^i h_a^j - \sum_b \rho_a^b h_b^i \\ &+ \frac{1}{2} \left[\sum_{prs} \rho_{pr}^{is} u_{as}^{pr} - \sum_{rqs} \rho_{ar}^{qs} u_{qs}^{ir} \right], \quad (34c) \end{aligned}$$

$$\begin{aligned} -i\hbar \sum_{bj} A_{bi}^{ja} \eta_j^b &= \sum_b \rho_b^a h_i^b - \sum_j \rho_i^j h_j^a \\ &+ \frac{1}{2} \left[\sum_{prs} \rho_{pr}^{as} u_{is}^{pr} - \sum_{rqs} \rho_{ir}^{qs} u_{qs}^{ar} \right]. \quad (34d) \end{aligned}$$

Finally, the Q -space orbital equations are

$$\begin{aligned} i\hbar \sum_q \rho_p^q Q \frac{\partial}{\partial t} |\varphi_q\rangle &= \sum_q \rho_p^q Q h |\varphi_q\rangle + \sum_{qrs} \rho_{pr}^{qs} Q W_s^r |\varphi_q\rangle, \quad (34e) \\ -i\hbar \sum_p \rho_p^q \left(\frac{\partial}{\partial t} \langle \tilde{\varphi}_p | \right) Q &= \sum_p \rho_p^q \langle \tilde{\varphi}_p | h Q + \sum_{prs} \rho_{pr}^{qs} \langle \tilde{\varphi}_p | W_s^r Q. \end{aligned} \quad (34f)$$

The right-hand sides of Eqs. (34a) and (34b) are *identical* to the one used in standard CCD calculations for the ground state energy, since the operator D_0 is eliminated due to $\rho_i^i = \rho_a^a = 0$, see Eq. (27b).

Since D_0 drops from (34a) and (34b), the right-hand sides can be evaluated independently of Eqs. (34c)–(34f). In order to evaluate $\tilde{\Phi}$ and Φ , η must be solved for in addition

to $Q|\phi_q\rangle$ and $\langle \tilde{\phi}_p | Q$. The results are assembled according to Eq. (29).

The Q -space equation for $|\phi_p\rangle$ is formally *identical* to the orbital equation of MCTDHF (see derivation in the Appendix), and the equation for $\langle \tilde{\phi}_p |$ is formally identical to the complex conjugate. However, in the CC case the matrices u_{pr}^{qs} , h_q^p , and ρ_p^q are *not exactly Hermitian*. Therefore, the two equations are only complex conjugates of each other to within an approximation, and both must be propagated.

F. Computational cost of OATDCCD

We will now consider the computational cost of evaluating the time derivatives in a computer implementation. We will in the following assume a grid-based discretization of single-particle space using in total N_b points. In particular, integrals are evaluated as sums with N_b elements.

We consider first the computation of the amplitude equations (34a) and (34b), assuming that h_q^p , etc., are available in computer memory. It is easy to see, from Eqs. (A7) and (A12), that by brute-force summation the worst-scaling terms require $O(N^4(L - N)^4) = O(L^8)$ operations for computing the totality of derivatives, which is a conservative estimate since $N < L$. Existing CC codes typically reduce this to $O(L^6)$ by clever use of intermediate variables.¹⁶

The P -space orbital equations (34c) and (34d) are linear equations where a vector of dimension $O(L^2)$ is to be solved for. This requires at most $O(L^6)$ operations. The right-hand side is dominated by the two-body terms, which cost $O(L^5)$ in total to compute.

We next turn to the Q -space orbital equations (34e) and (34f), which can be viewed as differential equations for matrices of dimension $N_b \times L$ and $L \times N_b$, respectively. The cost analysis is identical for the two. The matrix ρ_p^q needs to be inverted, a step of at most $O(L^3)$ cost. Multiplying Eq. (34e) by the inverse matrix elements of ρ_p^q shows that the Q -part of $i\hbar |\dot{\phi}_p\rangle$ can be computed as the sum of $Qh|\phi_p\rangle$ and a two-body mean-field term which clearly dominates the computation. The cost of this term is $O(L^3 N_b)$ plus $O(L^2 N_b)$ for the multiplication of the result with ρ^{-1} .

The one- and two-electron integrals h_q^p and u_{qs}^{pr} must be updated *at each time* t . This is similar to the situation in MCTDHF theory, and one can expect this to be a major time-consuming part of the propagation. Moreover, Eqs. (34c)–(34f) are formulated in terms of the reduced one- and two-electron matrices which need to be computed.

These matrix elements ρ_p^q and ρ_{ps}^{qr} cost less than the evaluation of the orbital equations right-hand sides in total, and h_q^p is relatively cheap to compute. However, the two-electron integrals and the mean-field functions W_s^r are costly. The computation of all the mean-fields, which are local functions, costs $O(L^2 N_b^2)$. Since $u_{qs}^{pr} = \langle \tilde{\varphi}_p | W_s^r | \varphi_q \rangle$, the computation of the two-electron integrals costs an additional $O(L^4 N_b)$ operation.

The computation of W_s^r is in fact very expensive, being similar in cost to computing two-particle integrals, i.e., six-dimensional integrals in realistic calculations. This problem is ubiquitous for all time-dependent mean-field calculations, and

a common approach to squeeze down the cost is to employ some low-rank expansion for the interaction potential $u(x, x')$, which needs to be sampled at the grid points $\xi_k, k = 1, \dots, N_b$. The resulting matrix $v(\xi_k, \xi_{k'})$ is symmetric, with eigenvalue decomposition

$$v(\xi_k, \xi_{k'}) = \sum_{m=1}^{N_b} \lambda_m f_m(\xi_k) f_m(\xi_{k'}), \quad (35)$$

where f_m is the eigenvector belonging to λ_m , the latter arranged in decreasing order. The optimal (in the 2-norm) M -term approximation to $v(\xi_k, \xi_{k'})$ is then obtained by truncating Eq. (35) after M terms. Oftentimes, only a small number $M \ll N_b$ terms are needed. Moreover, if N_b is increased, M may typically be held fixed. The mean-fields then become

$$W_s^r(\xi_k) \approx \sum_{m=1}^M \lambda_m v_m(\xi_k) \langle \tilde{\varphi}_r | v_m | \varphi_s \rangle,$$

which reduces the cost of computing W_s^r to $O(N_b L^2)$ for the inner products plus $O(L^2 N_b M)$ for the summation, reducing the cost proportionally to the fraction M/N_b of modes included in Eq. (35).

To sum up, we see that the cost of evaluating the right-hand sides of the equations of motion is dominated on one hand by the computation of the W_s^r and u_{ps}^{qr} and on the other hand by the evaluation of the amplitude equations, the latter costing $O(N^4(L - N)^4)$ (if no optimization is done). The amplitude equations scale much more gently with N than does the MCTDHF amplitude equations whose cost is *exponential* in N . The mean-fields cost about the same in both approaches, however.

It is easy to see, that with a given amount of processing power available, the number of particles treated may be substantially higher with OATDCCD compared to MCTDHF. As a numerical example, consider $L = 40$ and $N = 20$, giving 1.4×10^{11} coefficients A_μ in MCTDHF. This is very demanding. In contrast, the number of amplitudes in CCD is a modest 8×10^4 . Note that the complexity of the mean-fields is roughly the same in both cases.

IV. FURTHER PROPERTIES OF OATDCC

A. Relations to other methods

It is instructive to consider special cases of the OATDCC method and relate these to other, well-known wavefunction approximations.

In the case where *all* excitation levels are included, the CC ansatz becomes the FCI ansatz within the chosen basis. Therefore, the MCTDHF and OATDCC methods are equivalent in this limit.

At the other end of the hierarchy, we find the trivial case where there are no amplitudes at all, i.e., we take $L = N$ and $\Lambda = T = 0$. In that case, the OATDCC energy expectation

functional becomes

$$\begin{aligned} \mathcal{E}_H[\Phi, \tilde{\Phi}] &= \langle \tilde{\Phi} | H | \Phi \rangle \\ &= \langle \tilde{\Phi} | \left(\sum_{pq} h_q^p c_p^\dagger \tilde{c}_q + \frac{1}{4} \sum_{pqrs} u_{qs}^{pr} c_p^\dagger c_r^\dagger \tilde{c}_s \tilde{c}_q \right) | \Phi \rangle \\ &= \sum_p \langle \tilde{\varphi}_p | h | \varphi_p \rangle + \frac{1}{2} \sum_{pr} \langle \tilde{\varphi}_p \tilde{\varphi}_r | u | \varphi_p \varphi_r \rangle_{AS}. \end{aligned}$$

This is the variational Hartree–Fock energy functional (when $\tilde{\Phi} = \Phi^H$). The time-dependent action functional similarly gives the time-dependent Hartree–Fock (TDHF) variational functional, demonstrating equivalence between the trivial OATDCC and TDHF.

We also note that the OATDCCD approximation is equivalent to MCTDHF whenever $N = 2$. Moreover, some combinations of L and N also give equivalence, for example, $L = N + 2$ since there are no triple excitations defined.

Finally, in the absence of interactions, the Hamiltonian is a pure one-body Hamiltonian. One can easily show that the choice $i\hbar\dot{\Phi} = H\Phi$, $-i\hbar\dot{\tilde{\Phi}} = \tilde{\Phi}H$ and $\dot{\lambda}_\mu = \dot{\tau}^\mu = 0$ gives $\mathcal{S}[\lambda, \tau, \tilde{\Phi}, \Phi] = 0$ and a stationary \mathcal{S} . This is the *exact* solution to the dynamics for any initial condition. (The gauge conditions in this case are chosen differently from earlier: $\eta_j^i = \langle \tilde{\varphi}_i | \dot{\varphi}_j \rangle = \langle \tilde{\varphi}_i | H^{(1)} | \varphi_j \rangle / i\hbar$ and $\eta_b^a = \langle \tilde{\varphi}_a | H^{(1)} | \varphi_b \rangle / i\hbar$.)

As early as 1978, Hoodbhoy and Negele²⁰ discussed a time-dependent CC approach using an *explicit* dependence of time in the orthonormal single-particle functions. This would correspond to using the following functional to define the evolution

$$\begin{aligned} \mathcal{S}_{H-N}[\tau, \lambda] &= \int_0^T i\hbar \lambda_\mu \dot{\tau}^\mu - \langle \tilde{\Phi} | (1 + \Lambda) e^{-T} (H - i\hbar D_0(t)) e^T | \Phi \rangle dt. \quad (36) \end{aligned}$$

Here, the D_0 operator is simply a correction in the standard CC Lagrangian due to a moving basis. Hoodbhoy and Negele suggested computing the time-dependence of Φ using TDHF, i.e., a TDHF calculation is first performed, and the output is fed into \mathcal{S}_{H-N} . However, this approach would have inferior approximation properties compared to OATDCC while at the same time being only marginally easier to evolve in time. To see this, consider the fact that the TDHF solution would depend *only* on the initial choice of the orbitals, and *not* on the full state at time t as in the OATDCC approach. The OATDCC orbitals will generally differ substantially from the TDHF solution, since their motion is computed from the wavefunctions *at time t*. The Hoodbhoy–Negele TDHF approach neglects the correlation effects built into the wavefunction during the evolution. As for the computational cost, note that TDHF needs the computation of the two-particle integrals, so one gains very little, if nothing, at simplifying to TDHF for the orbitals.

B. Approximation properties

We now ask: what kinds of systems can we expect to be able to treat with OATDCC, and what systems cannot be expected to give good results?

The usual CC ansatz (with fixed orbitals) is based on a single-reference determinant, incorporating correlations through the cluster operator. For good results, the reference determinant should be a “large” part of the wavefunction. In the language of computational chemistry, dynamic correlation (which by definition is due to the interparticle interactions) must be dominating, while static correlation (arising from degeneracies in the spectrum) should be small.

For a *dynamical* calculation we must correspondingly require that, for all $t \geq 0$, the wavefunction is a single-reference type state. This is reasonable whenever the *initial condition* is of such type: intuitively, the Hamiltonian cannot generate static correlation since the only source of correlation from dynamics is the interparticle interaction. This is actually observed in the numerical experiment in Sec. V.

However, standard CC is known to perform adequately even in the presence of static correlation, which gives reason to believe that the same holds true for OATDCC calculations.

It is worthwhile to note that for systems with spin, the OATDCC ansatz is not an eigenfunction of the total spin; only of the total spin projection along some preselected direction in space z . This is, however, not a problem in general if H commutes with total spin: all expectation values for spin-independent observables are the same as for the properly “spin-symmetrized” wavefunction.

C. Non-feasibility of imaginary time relaxation

Regarding the choice of initial conditions for OATDCC, one would typically like to start in the ground state of the system under consideration, or a state closely related to this. Indeed, the orbital-adaptive CC ansatz could in principle be used for ground state calculations in the first place, just like MCTDHF actually is a time-dependent version of the multi-configuration Hartree–Fock for computing eigenvalues of H .

The ground state is a critical point for \mathcal{E}_H , and in standard variational theory this can be computed using imaginary time propagation, that is to say, formally replacing the time t with $-is$; so-called Wick rotation. Notice that the complex conjugate wavefunction propagates in “reverse imaginary time,” as is seen from the following equations:

$$i\hbar \frac{\partial}{\partial t} |\Psi\rangle = H |\Psi\rangle \rightarrow \hbar \frac{\partial}{\partial s} |\Psi\rangle = -H |\Psi\rangle, \quad (37a)$$

$$-i\hbar \frac{\partial}{\partial t} \langle\Psi| = \langle\Psi| H \rightarrow \hbar \frac{\partial}{\partial s} \langle\Psi| = -\langle\Psi| H. \quad (37b)$$

(For simplicity, we here consider the exact wavefunctions.)

Since the variational energy is bounded from below, and since $d\mathcal{E}_H/ds \leq 0$, a critical point of the variational energy is obtained as $s \rightarrow +\infty$. This is a quite robust procedure for variational approximations. For non-variational methods like coupled-cluster, the situation is, literally, more complex.

The most immediate concern is the fact that the energy is not bounded from below. Hence, even if $d\mathcal{E}_H/ds \leq 0$ it is not guaranteed to converge. But let us disregard this possible problem for the moment, and instead consider local coordinates $z(t) \in \mathbb{C}^n$ for a generic bivariational parametrization. Naïvely, one expects that propagating the equation of motion

(10) in imaginary time corresponds to Wick rotation, i.e.,

$$i\hbar C(z) \frac{\partial}{\partial t} z = \nabla_z E[z] \rightarrow \hbar C(z) \frac{\partial}{\partial s} z = -\nabla_z E[z]. \quad (38)$$

This is not the case! To see this, consider the bivariational formulation of a variational method: if $|\Psi\rangle$ is parametrized by some complex numbers u_k , then $\langle\Psi|$ is parametrized by $v_k = u_k^*$, i.e., $z = (v, u)$. The two components are treated as independent. Under bivariational Wick rotation, we saw that v should be propagated in *backwards* imaginary time, contrary to the imaginary time propagation of Eq. (38), where all coordinates are propagated forward.

Indeed, consider the fact that Eq. (10) is *analytic* in both the coordinates z and t . Thus, the energy is an *analytic* function of complex-valued time t . On the other hand, energy is conserved, $d\mathcal{E}[z(t)]/dt \equiv 0$. Thus, the energy is a constant analytic function. Performing the naïve Wick rotation on *all* the coordinates z_k corresponds to evaluating the wavefunction at a complex time, $-is$, and the energy does not decrease.

We conclude that a proper bivariational treatment of Wick rotation necessarily implies that variables are treated differently: In the simplest cases, we must identify one half of the coordinates to be propagated in forward imaginary time, and a second half to be propagated backward. This is not straightforward to achieve when the parametrizations of $|\Psi\rangle$ and $\langle\Psi|$ are not easily related, such as in the OATDCC method.

For constant orbitals, it is possible to propagate the τ^μ equation (34a) in imaginary time alone until a stationary point is found, i.e., λ_μ is ignored in the propagation, and instead computed afterwards from the usual stationary CC conditions for energy. (Note however, that since \mathcal{E}_H is not bounded from below, the energy is not guaranteed to converge.) This works because the equation of motion for τ^μ never involves λ_μ . Unfortunately, we do not know how to treat the orbitals in such an approach.

We conclude that computing the ground state using imaginary time propagation is not straightforward and requires separate study. Instead, quasi-Newton schemes like those already used for standard CC could be used, but we will not investigate this further in the present article.

Until such a recipe can be made, one suggestion presents itself as a good alternative: One may perform a Hartree–Fock calculation to generate a set of orbitals, and then perform a CCD calculation within this basis. This is the standard practice for molecular calculations, and even though not an *exact* critical point of the OATDCC energy, it should be a suitable starting point for dynamics calculations. In our numerical experiment in Sec. V, we choose a similar approach.

V. A NUMERICAL EXPERIMENT

A. Outline and model system

A numerical experiment on a model system mimicking electron-atom collision has been performed in order to test the OATDCCD method against the standard MCTDHF method and to check that the results are sensible. Generic MCTDHF and OATDCCD codes have been written from scratch. The

MCTDHF code was tested against numerical experiments reported in the literature⁸ and found to agree perfectly with these. The OATDCCD code uses the algebraic expressions listed in the Appendix for the equations of motion. The code is tested against MCTDHF computations for special combinations of L and N where the two ansätze are equivalent. Perfect agreement was found, indicating the correctness of the implementation.

Neither code is optimized, and note that since N is quite small, the asymptotic scaling of the CC method is not visible. The simulations all run in about 1 h on a standard desktop computer.

The numerical experiment consists of two phases: (1) preparation of the initial wavefunction, and (2) propagation of this state from $t = 0$ to $t = t_{\text{final}}$ using both MCTDHF and OATDCC while monitoring some observables. In particular, the energy \mathcal{E}_H should be conserved at all times.

The test system is defined as follows. Consider a model consisting of N electrons in one spatial dimension. The orbitals are functions $\varphi_p(x, s)$, where $x \in \mathbb{R}$ is the spatial position and $s \in \{-\frac{1}{2}, +\frac{1}{2}\}$ is the quantum number of the projection of the electron spin along some arbitrary axis.

The particles interact via a smoothed Coulomb force (for simplicity) and an external Gaussian well potential. The Hamiltonian of the system has one-body part

$$h = -\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x), \quad V(x) = -V_0 e^{-x^2/2a^2},$$

where $V_0 = 7$ and $a = 1.5$ are the parameters of the Gaussian well. The smoothed Coulomb interaction is given by

$$u(x_1, x_2) = \frac{\lambda}{\sqrt{|x_1 - x_2|^2 + \delta^2}},$$

and we use parameters $\lambda = 1$ and $\delta = 0.2$. These are reasonable parameters for, say, a quantum wire model.³⁴

The complete Hamiltonian is seen to commute with any spin operator. We remark that if (1) the initial orbitals are spin-orbitals of the form $\varphi_p(x, s) = \psi_p(x) \chi_{\sigma_p}(s)$, where χ_{σ} is a spinor basis function, and if (2) the initial wavefunction is an eigenfunction for the *total* spin projection operator, the equations of motion (34) preserve these properties. That is to say, under these conditions the orbitals are always on product form

$$\varphi_p(x, s, t) = \psi_p(x, t) \chi_{\sigma_p}(s),$$

and the wavefunction remains an eigenfunction of the total spin projection.

B. Discretization and propagation scheme

We discretize the one-particle coordinates by introducing a standard discrete Fourier transform-based discretization over the interval $[-R, R]$ using $N_{\text{grid}} = 64$ points.³⁵ The total number of basis functions is then $N_b = 2N_{\text{grid}} = 128$. The kinetic energy operator is evaluated using the fast Fourier transform and is highly efficient and accurate. In our calculations, we set $R = 15$. The orbital matrices $\tilde{\Phi}$ and Φ become standard matrices of dimension $L \times N_b$ and $N_b \times L$, respectively, giving a simple representation in the computer code.

For propagation, we choose a variational splitting scheme.³⁶ Variational splitting is a generalization of the standard split-step scheme used for brute-force grid discretizations of few-body problems.³⁵ Using this scheme, the time step Δt can be chosen relatively large and independently of the grid spacing Δx . Variational splitting is most easily described in terms of a *time-dependent* Hamiltonian $\hat{H}(t) = T + \sum_{n=-\infty}^{\infty} \delta(t - (n + 1/2)\Delta t)(H - T)$, where T is the kinetic energy operator and $H - T$ is the remaining potential terms. A time step then consists of three steps: (1) Propagation using kinetic energy *only* a time step $\Delta t/2$, (2) propagation using $H - T$ *only* a time step Δt using a fourth order Runge–Kutta for simplicity, and finally (3) step (1) is repeated. The key point is that the stability of the scheme becomes insensitive to Δx , and that step (1) is evaluated exactly without involving the amplitudes at all. The local error is of order Δt^3 . A simple integration of Eqs. (34) using, say, Runge–Kutta will require a time step $\Delta t \sim \Delta x^2$. In multi-configurational time-dependent Hartree calculations, other ways of eliminating this stability problem than variational splitting is often used, e.g., the constant mean-field scheme.² However, this requires more coding effort than variational splitting which is sufficient for our modest purposes.

C. Preparation of initial wavefunction

We need initial wavefunctions for both the MCTDHF and OATDCCD ansätze allowing sensible comparison. The former is computed as follows.

The parameters of the Gaussian well potential and interaction potential are experimentally chosen so that they support an $N = 4$ ground state $|\Psi_4\rangle$ with total spin projection zero. This ground state is computed in the MCTDHF scheme using imaginary time propagation of the equations of motion from a random initial condition.

In order to generate non-trivial but easily understood dynamics, we prepare a fifth particle in a classical-like Gaussian wavepacket $g(x, s)$ given by

$$g(x, s) = C \exp[-(x - x_0)^2/(4\sigma^2) + ik_0 x] \chi_{+1/2}(s),$$

where C is a normalization constant, x_0 the “starting position” of the particle, and k_0 is the “starting momentum.” The parameter σ controls the width of the wavepacket. For our experiment, we choose $x_0 = 10$, $k_0 = 1.2$, and $\sigma = 1.25$. Note that we (arbitrarily) choose spin $+1/2$ for this particle. The initial MCTDHF state is then

$$|\Psi\rangle = g^\dagger |\Psi_4\rangle,$$

where g^\dagger is the creation operator associated with $g(x, s)$. The complete wavefunction therefore intuitively describes an incoming electron on collision course with a bound beryllium-like “atom” in the ground state.

In terms of the MCTDHF parameters, the addition of the particle simply corresponds to extending the orbital matrix Φ with an extra column (orthogonalized against the others), in addition to a lot of zeroes in the MCTDHF coefficient vector A .

The spatial particle density $n(x) = n(x, -1/2) + n(x, +1/2)$ of $|\Psi\rangle$ is shown in Fig. 1 along with the confining

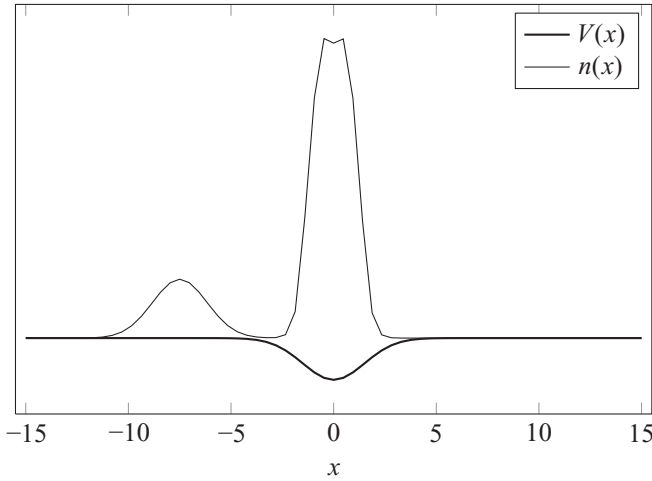


FIG. 1. Particle density $n(x)$ of initial wavefunction and Gaussian well $V(x)$. Units are arbitrary.

potential. The spin-density $n(x, s)$ is given by the diagonal of the reduced one-body density matrix $\gamma(x, s, x', s')$, viz,

$$\gamma(x', s', x, s) = \langle \Psi | \psi^\dagger(x, s) \psi(x', s') | \Psi \rangle,$$

or in terms of the coefficients $\rho^{(1)} = [\rho_p^q]$ and the orbitals,

$$\gamma = \Phi \rho^{(1)} \Phi^H. \quad (39)$$

Having obtained the MCTDHF initial wavefunction, the OATDCCD initial condition is computed as follows. We first transform the orthonormal orbitals Φ to generate orthonormal so-called Brueckner orbitals Φ_B . The wavefunction amplitudes are transformed accordingly. By definition,³⁷ the Brueckner orbitals optimize the overlap with the reference determinant, which is actually equivalent to the convenient property that the singles amplitudes vanish identically, the so-called Brillouin–Brueckner theorem. We now have

$$|\Psi\rangle = \langle \phi_B | \Psi \rangle (1 + A_2 + A_3 + \dots) | \phi_B \rangle = \langle \phi_B | \Psi \rangle e^{T_2 + T_3 + \dots} | \phi_B \rangle, \quad (40)$$

where $|\phi_B\rangle$ is the determinant that has maximum overlap with $|\Psi\rangle$. We now simply take the OATDCC orbitals at $t = 0$ to be Φ_B (and $\tilde{\Phi} = \Phi_B^H$), and let T_2 be as in Eq. (40), i.e., we perform a projection in CC amplitude space.

It remains to define Λ_2 . We note that for the MCTDHF limit of OATDCC, $\langle \tilde{\Psi} | = \langle \Psi | / \langle \Psi | \Psi \rangle$, which gives Λ_n such that

$$\langle \tilde{\Psi} | e^{T_2^\dagger + T_3^\dagger + \dots} = \langle \phi_B | (1 + \Lambda_1 + \Lambda_2 + \dots),$$

which is used to extract Λ_2 algebraically in the computer code.

We comment that the initial condition computed in this way only is a critical point of the coupled cluster energy to within an approximation, albeit a very good one. Alternatively, we could solve the CCD equations in the Brueckner basis, which gives very similar results.

We comment that the OATDCC counterpart of the density matrix (39) is

$$\gamma = \Phi \rho^{(1)} \tilde{\Phi}. \quad (41)$$

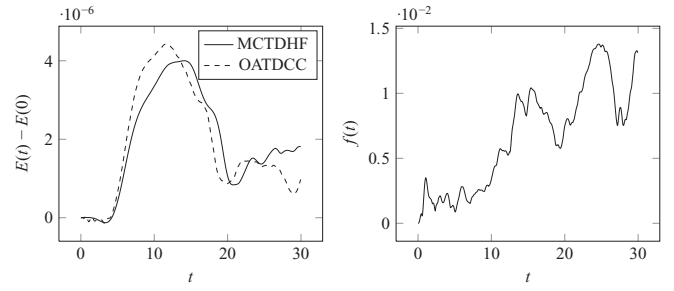


FIG. 2. (Left) Energy conservation in the MCTDHF and OATDCCD schemes for the numerical experiment. The deviation from the initial energy is shown. The initial energies are $E_{\text{MCTDHF}}(0) = -12.2102145$ and $E_{\text{OATDCCD}}(0) = -12.2104173$. The gap between these numbers are due to neglect of the triples amplitudes and higher in the ground state. (Right) Integral of imaginary part of particle density, see Eq. (42).

The density plot of the OATDCC initial condition is visually indistinguishable from the MCTDHF initial condition, so we do not plot it separately in Fig. 1.

D. Results

Having obtained initial conditions, these are propagated in time with $\Delta t = 0.005$ until $t = t_{\text{final}} = 30$. The energy is conserved to a very high precision, see Fig. 2. The energy-conservation also improves with reduced time step, as is expected.

As discussed in Sec. II B, expectation values may gain small imaginary parts. Along the CC computation, we therefore monitor

$$f(t) = \sum_s \int |\text{Im } n(x, s, t)| dx. \quad (42)$$

In Fig. 2 $f(t)$ is displayed, and it is indeed a small number compared to the particle number $N = 5$.

In Fig. 3, we show the density as function of t of each calculation side by side. They are seen to agree qualitatively. The density evolution clearly shows how the incident electron interacts with the beryllium “atom.” Some of the density is transmitted and reflected from the atom, while the atom is slightly perturbed, performing small amplitude oscillations. This demonstrates that many-body effects in the simulation are significant, and that the OATDCCD calculation captures these well.

Quantitatively, the densities show some differences after the collision event that may look like a phase shift in the oscillation of the atom part. We have not investigated further, but conjecture this to be a result of the fact that the CC approximation changes the spectrum slightly. The absolute value of the density difference is shown in Fig. 4.

VI. CONCLUSION AND OUTLOOK

The bivariational principle for Schrödinger dynamics has been discussed at length, and the OATDCC method was developed. The method can be viewed as a systematic hierarchy of approximations to the highly successful MCTDHF method for fermions, with simple time-dependent Hartree–Fock as the simplest case. The OATDCCD method was discussed in

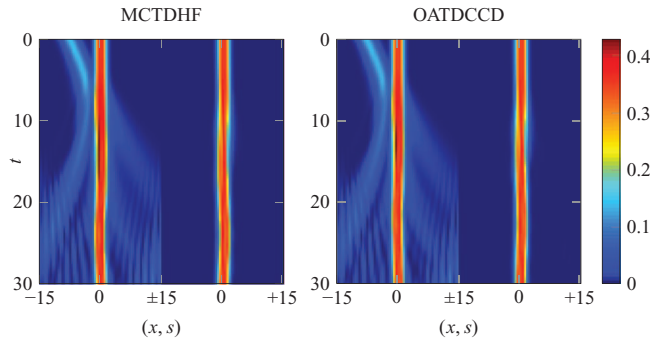


FIG. 3. Electron density plot as function of time for each calculation. MCTDHF is on the left, while OATDCC is on the right. The x axis is divided into spin up (left half) and spin down (right half). The two densities are seen to be very similar, see also Fig. 4. The incident electron is clearly reflected and partially transmitted through the initially stationary beryllium atom. After the collision, the atom is seen to exhibit oscillations. The interference fringes at the end of the simulations are due to boundary effects.

detail, and a numerical experiment performed showing that the method gives sensible results. The OATDCC scales polynomially where MCTDHF scales exponentially with the number of particles N . The complexity of the mean-field calculations are the same in the two methods.

The method may be particularly useful for systems whose state is unbound. Examples include atoms under the influence of time-dependent external electromagnetic fields.

It was observed that imaginary time propagation for eigenvalue computation does not seem feasible for the OATDCC method. Methods for solving the time-independent orbital-adaptive CC should be studied. Such an eigenvalue computation method would constitute a hierarchy of approximations to the multi-configurational Hartree–Fock method.

The OATDCC is easily generalized to bosonic systems, with possibly interesting applications to Bose–Einstein condensates, for which CC has a particularly simple form: The CC ansatz naturally captures the idea of excitations on top of a condensate.³⁸ The resulting method will approximate the MCTDH method for bosons,⁴ and can treat substantially more particles since the dimensionality reduction for bosons is much greater than for fermions. For example, we have $O(L^2)$ CCD amplitudes vs. $O(L^N)$ MCTDH coefficients.

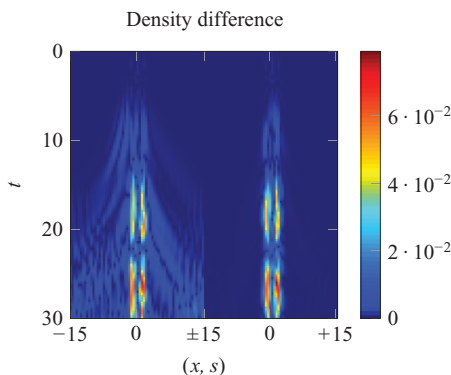


FIG. 4. Differences between the OATDCC and MCTDHF electron densities calculated. The main feature is a phase-shift in the atom oscillations.

Further possible lines of research include generalizations to multireference CC theory for systems with a large degree of static correlation, and studying Arponen’s extended CC method,¹¹ where $\langle \tilde{\Psi} |$ is parametrized as $\langle \tilde{\phi} | \exp(T') \exp(-T)$, where T' is a de-excitation operator. For structure calculations, extended CC includes orders of magnitude more Feynman diagrams to the ground state energy compared to standard CC, at the cost of higher polynomial complexity. For OATDCC, this indicates a much higher accuracy of the functionals \mathcal{E}_H and \mathcal{S} , while retaining a modest scaling with the number of particles.

ACKNOWLEDGMENTS

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APPENDIX A: ALGEBRAIC EXPRESSIONS FOR CCD

Here, we list algebraic expressions for various quantities appearing in the OATDCC method using a doubles only ansatz, i.e., CCD. The expressions are computed using the second quantization toolbox in the PYTHON library SYMPY.²³ Expressions are thoroughly checked against standard references.^{10,16}

The expression for the expectation functional is

$$\mathcal{E}_H[\lambda, \tau, \tilde{\Phi}, \Phi] = \langle \tilde{\phi} | H e^T | \phi \rangle + \sum_{\mu} \lambda_{\mu} \frac{\partial}{\partial \lambda_{\mu}} \mathcal{E}_H[\lambda, \tau, \tilde{\Phi}, \Phi] \quad (\text{A1})$$

$$= \langle \tilde{\phi} | H e^T | \phi \rangle + \sum_{\mu} \lambda_{\mu} \langle \tilde{\phi}_{\mu} | e^{-T} H e^T | \phi \rangle \quad (\text{A2})$$

$$= \langle \tilde{\phi} | H e^T | \phi \rangle + \frac{1}{4} \sum_{ijab} \lambda_{ij}^{ab} \langle \tilde{\phi}_{ij}^{ab} | e^{-T} H e^T | \phi \rangle, \quad (\text{A3})$$

where we have used linearity of \mathcal{E}_H in λ_{μ} , and where the latter expression explicitly states the expansion in the CCD case.

To obtain computational formulae, we consider separately the one- and two-body terms in H , i.e.,

$$H^{(1)} = \sum_{pq} h_q^p c_p^{\dagger} \tilde{c}_q, \quad h_q^p = \langle \tilde{\phi}_p | H^{(1)} | \phi_q \rangle \quad (\text{A4})$$

and

$$H^{(2)} = \frac{1}{4} \sum_{pqrs} u_{qs}^{pr} c_p^{\dagger} c_r^{\dagger} \tilde{c}_s \tilde{c}_q, \quad u_{qs}^{pr} = \langle \tilde{\phi}_p \tilde{\phi}_r | H^{(2)} | \phi_q \phi_s \rangle_{AS}. \quad (\text{A5})$$

The coefficients u_{qs}^{pr} are the the anti-symmetrized two-body integrals, see Eqs. (16a) and (16b). We get

$$\langle \tilde{\phi} | H^{(1)} e^T | \phi \rangle = h_i^i \quad (\text{A6a})$$

$$\langle \tilde{\phi} | H^{(2)} e^T | \phi \rangle = \frac{1}{4} \tau_{ij}^{ab} u_{ab}^{ij} + \frac{1}{2} u_{ij}^{ij} \quad (\text{A6b})$$

for the CCD energy, and

$$\frac{\partial}{\partial \lambda_{ab}^{ij}} \mathcal{E}_{H^{(1)}} = -h_c^a \tau_{ij}^{bc} P(ab) + h_i^k \tau_{jk}^{ab} P(ij) \quad (\text{A7a})$$

$$\begin{aligned} \frac{\partial}{\partial \lambda_{ab}^{ij}} \mathcal{E}_{H^{(2)}} = & -\tau_{ik}^{ab} u_{jl}^{kl} P(ij) + \frac{1}{2} \tau_{il}^{ab} \tau_{jk}^{dc} u_{dc}^{kl} P(ij) + \frac{1}{4} \tau_{kl}^{ab} \tau_{ij}^{dc} u_{dc}^{kl} \\ & + \frac{1}{2} \tau_{kl}^{ab} u_{ij}^{kl} + \frac{1}{2} \tau_{ij}^{ac} \tau_{kl}^{bd} u_{dc}^{kl} P(ab) \\ & + \tau_{ij}^{ac} u_{ck}^{bk} P(ab) - \tau_{ik}^{ac} \tau_{jl}^{bd} u_{dc}^{kl} P(ab) \\ & + \tau_{ik}^{ac} u_{jc}^{bk} P(ab) P(ij) + \frac{1}{2} \tau_{ij}^{dc} u_{dc}^{ab} + u_{ij}^{ab} \end{aligned} \quad (\text{A7b})$$

for the derivatives with respect to λ_{ab}^{ij} . The operator $P(ij)$ is an anti-symmetrizer: $f(ij)P(ij) = f(ij) - f(ji)$, and similarly for $P(ab)$. The appearance of a $P(ij)$ or a $P(ab)$ should be ignored for the invocation of the summation convention.

Inserting these expressions back into Eq. (A1), the complete expression for the CCD expectation value functional becomes

$$\begin{aligned} \mathcal{E}_H[\lambda, \tau, \tilde{\Phi}, \Phi] = & \frac{1}{2} h_b^a \lambda_{ac}^{ij} \tau_{ij}^{bc} + h_i^i - \frac{1}{2} h_i^j \lambda_{ab}^{ki} \tau_{kj}^{ab} \\ & - \frac{1}{2} \lambda_{ab}^{ij} \tau_{ki}^{ab} u_{lj}^{kl} + \frac{1}{8} \lambda_{ab}^{ij} \tau_{kj}^{ab} \tau_{li}^{dc} u_{dc}^{kl} \\ & + \frac{1}{16} \lambda_{ab}^{ij} \tau_{kl}^{ab} \tau_{ij}^{dc} u_{dc}^{kl} + \frac{1}{8} \lambda_{ab}^{ij} \tau_{kl}^{ab} u_{ij}^{kl} \\ & + \frac{1}{8} \lambda_{ab}^{ij} \tau_{li}^{ab} \tau_{kj}^{dc} u_{dc}^{kl} + \frac{1}{2} \lambda_{ab}^{ij} \tau_{ij}^{ac} u_{ck}^{bk} \\ & + \lambda_{ab}^{ij} \tau_{ki}^{ac} u_{cj}^{bk} - \frac{1}{2} \lambda_{ab}^{ij} \tau_{kj}^{ac} \tau_{li}^{db} u_{dc}^{kl} \\ & - \frac{1}{4} \lambda_{ab}^{ij} \tau_{kl}^{ac} \tau_{ij}^{db} u_{dc}^{kl} + \frac{1}{8} \lambda_{ab}^{ij} \tau_{ij}^{dc} u_{dc}^{ab} + \frac{1}{4} \lambda_{ab}^{ij} u_{ij}^{ab} \\ & + \frac{1}{4} \tau_{ij}^{ab} u_{ab}^{ij} + \frac{1}{2} u_{ij}^{ij}. \end{aligned} \quad (\text{A8})$$

To solve the equations of motion for the amplitudes λ_{ab}^{ij} , we also need the derivatives of \mathcal{E}_H with respect to τ_{ij}^{ab} . For the one-body part

$$\frac{\partial}{\partial \tau_{ij}^{ab}} \mathcal{E}_{H^{(1)}} = h_k^i \lambda_{ab}^{jk} P(ij) - h_a^c \lambda_{bc}^{ij} P(ab), \quad (\text{A9a})$$

and for the two-body part,

$$\begin{aligned} \frac{\partial}{\partial \tau_{ij}^{ab}} \mathcal{E}_{H^{(2)}} = & -\frac{1}{2} \lambda_{bc}^{ij} \tau_{kl}^{dc} u_{ad}^{kl} P(ab) - \lambda_{bc}^{ij} u_{ak}^{ck} P(ab) \\ & + \frac{1}{4} \lambda_{dc}^{ij} \tau_{kl}^{dc} u_{ab}^{kl} + \frac{1}{2} \lambda_{dc}^{ij} u_{ab}^{dc} + \frac{1}{2} \lambda_{ab}^{jk} \tau_{kl}^{dc} u_{dc}^{il} P(ij) \\ & + \lambda_{ab}^{jk} u_{kl}^{il} P(ij) - \lambda_{bc}^{jk} \tau_{kl}^{dc} u_{ad}^{il} P(ab) P(ij) \\ & + \lambda_{bc}^{jk} u_{ak}^{ic} P(ab) P(ij) + \frac{1}{2} \lambda_{dc}^{jk} \tau_{kl}^{dc} u_{ab}^{il} P(ij) \\ & + \frac{1}{4} \lambda_{ab}^{kl} \tau_{kl}^{dc} u_{dc}^{ij} + \frac{1}{2} \lambda_{ab}^{kl} u_{kl}^{ij} \\ & - \frac{1}{2} \lambda_{bc}^{kl} \tau_{kl}^{dc} u_{ad}^{ij} P(ab) + u_{ab}^{ij}. \end{aligned} \quad (\text{A9b})$$

Our calculations for expectation values and derivatives are of course valid for any one- or two-body operator.

Expressions for the reduced density matrices ρ_p^q are readily obtained from $\mathcal{E}_{H^{(1)}}$ by using $h_{q'}^{p'} = \delta_{p'}^{q'} \delta_{q'}^q$. We get $\rho_i^a = \rho_a^i = 0$, while

$$\rho_i^j = \mathcal{E}_{c_i^\dagger \tilde{c}_j} = \delta_i^k \delta_k^j - \frac{1}{2} \delta_i^l \delta_m^j \lambda_{ab}^{kl} \tau_{km}^{ab} = \delta_i^j - \frac{1}{2} \lambda_{ab}^{kj} \tau_{ki}^{ab}, \quad (\text{A10a})$$

$$\rho_a^b = \mathcal{E}_{c_a^\dagger \tilde{c}_b} = \frac{1}{2} \delta_a^d \delta_e^b \lambda_{dc}^{ij} \tau_{ij}^{ec} = \frac{1}{2} \lambda_{ac}^{ij} \tau_{ij}^{bc}. \quad (\text{A10b})$$

We comment that ρ_i^a and ρ_a^i can be seen to vanish from more basic considerations

$$\rho_a^i = \langle \tilde{\phi} | (1 + \Lambda) e^{-T} c_a^\dagger \tilde{c}_i e^T | \phi \rangle = \langle \tilde{\phi} | (1 + \Lambda) c_a^\dagger \tilde{c}_i | \phi \rangle = \lambda_a^i = 0, \quad (\text{A11})$$

since $c_a^\dagger \tilde{c}_i$ is an excitation operator and since all singles are eliminated. Moreover, note that $e^{-T_2} c_i^\dagger \tilde{c}_a e^{T_2} | \phi \rangle$ is *at least* triply excited. Hence, for the CCD approximation

$$\rho_i^a = \langle \tilde{\phi} | (1 + \Lambda_2) e^{-T} c_i^\dagger \tilde{c}_a e^T | \phi \rangle = 0. \quad (\text{A12})$$

Finally, we compute the two-body reduced density matrix. We only list nonzero elements

$$\rho_{ij}^{kl} = P(ij) \delta_i^k \delta_j^l - P(ij) P(kl) \frac{1}{2} \delta_i^k \lambda_{cd}^{lm} \tau_{jm}^{cd} + \frac{1}{2} \lambda_{cd}^{kl} \tau_{ij}^{cd}, \quad (\text{A13a})$$

$$\begin{aligned} \rho_{ij}^{ab} = & -P(ab) \frac{1}{2} \lambda_{cd}^{kl} \tau_{ij}^{ac} \tau_{kl}^{bd} + P(ij) \lambda_{cd}^{kl} \tau_{ik}^{ac} \tau_{jl}^{bd} \\ & + P(ij) \frac{1}{2} \lambda_{cd}^{kl} \tau_{il}^{ab} \tau_{jk}^{cd} + \frac{1}{4} \lambda_{cd}^{kl} \tau_{kl}^{ab} \tau_{ij}^{cd} + \tau_{ij}^{ab}, \end{aligned} \quad (\text{A13b})$$

$$\rho_{ia}^{jb} = -\rho_{ia}^{bj} = -\rho_{ai}^{jb} = \rho_{ai}^{bj} = \frac{1}{2} \delta_i^j \lambda_{ac}^{kl} \tau_{kl}^{bc} - \lambda_{ac}^{jk} \tau_{ik}^{bc}, \quad (\text{A13c})$$

$$\rho_{ab}^{ij} = \lambda_{ab}^{ij}, \quad \rho_{ab}^{cd} = \frac{1}{2} \lambda_{ab}^{ij} \tau_{ij}^{cd}. \quad (\text{A13d})$$

¹Multidimensional Quantum Dynamics: MCTDH Theory and Applications, edited by H.-D. Meyer, F. Gatti, and G. A. Worth (Wiley, 2009).

²M. H. Beck, A. Jäckle, G. A. Worth, and H.-D. Meyer, *Phys. Rep.* **324**, 1 (2000).

- ³H.-D. Meyer, U. Manthe, and L. S. Cederbaum, *Chem. Phys. Lett.* **165**, 73 (1990).
- ⁴O. E. Alon, A. I. Streltsov, and L. S. Cederbaum, *Phys. Rev. A* **77**, 033613 (2008).
- ⁵J. Broeckhove, L. Lathouwers, E. Kesteloot, and P. Van Leuven, *Chem. Phys. Lett.* **149**, 547 (1988).
- ⁶P. Kramer and M. Saraceno, *Geometry of the Time-Dependent Variational Principle* (Springer, 1981).
- ⁷C. Lubich, *Math. Comput.* **74**, 765 (2005).
- ⁸J. Zanghellini, M. Kitzler, T. Brabec, and T. Scrinzi, *J. Phys. B: At. Mol. Opt. Phys.* **37**, 763 (2004).
- ⁹T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, 2002).
- ¹⁰I. Shavitt and R. J. Bartlett, *Many-Body Methods in Chemistry and Physics: MBPT and Coupled-Cluster Theory* (Cambridge, 2009).
- ¹¹J. Arponen, *Ann. Phys.* **151**, 311 (1983).
- ¹²E. Dalgaard and H. J. Monkhorst, *Phys. Rev. A* **28**, 1217 (1983).
- ¹³T. Helgaker and P. Jørgensen, *Theor. Chim. Acta* **75**, 111 (1989).
- ¹⁴H. Koch and P. Jørgensen, *J. Chem. Phys.* **93**, 3333 (1990).
- ¹⁵T. B. Pedersen, B. Fernandez, and H. Koch, *J. Chem. Phys.* **114**, 6983 (2001).
- ¹⁶T. D. Crawford, *Rev. Comput. Chem.* **14**, 33 (2000).
- ¹⁷R. J. Bartlett and M. Musiał, *Rev. Mod. Phys.* **79**, 291 (2007).
- ¹⁸F. E. Harris, H. Monkhorst, and D. L. Freeman, *Algebraic and Diagrammatic Methods in Many-Fermion Theory* (Oxford, 1992).
- ¹⁹K. Schönhammer and O. Gunnarsson, *Phys. Rev. B* **18**, 6606 (1978).
- ²⁰P. Hoodbhoy and J. W. Negele, *Phys. Rev. C* **18**, 2380 (1978).
- ²¹P. Hoodbhoy and J. W. Negele, *Phys. Rev. C* **19**, 1971 (1979).
- ²²C. Huber and T. Klamroth, *J. Chem. Phys.* **134**, 054113 (2011).
- ²³SymPy Development Team, SymPy: Python library for symbolic mathematics, 2009.
- ²⁴See supplementary material at <http://dx.doi.org/10.1063/1.4718427> for further mathematical appendices.
- ²⁵R. Schneider, *Numer. Math.* **113**, 433 (2009).
- ²⁶T. Rohwedder, "The continuous coupled cluster formulation for the electronic Schrödinger equation," *Math. Modell. Numer. Anal.* (submitted).
- ²⁷T. Rohwedder and R. Schneider, "Error estimates for the coupled cluster method," *Math. Modell. Numer. Anal.* (submitted).
- ²⁸O. Koch and C. Lubich, *Math. Modell. Numer. Anal.* **41**, 315 (2007).
- ²⁹D. Conte and C. Lubich, *Math. Modell. Numer. Anal.* **44**, 759 (2010).
- ³⁰C. Bardos, I. Catto, N. Mauser, and S. Trabelsi, *Arch. Ration. Mech. Anal.* **198**, 273 (2010).
- ³¹P.-O. Löwdin, P. Froelich, and M. Mishra, *Int. J. Quantum Chem.* **36**, 93 (1989).
- ³²J. Killingbeck, *Rep. Prog. Phys.* **40**, 963 (1977).
- ³³G. C. Wick, *Phys. Rev.* **80**, 268 (1950).
- ³⁴S. M. Reimann and M. Manninen, *Rev. Mod. Phys.* **74**, 1283 (2002).
- ³⁵H. Tal-Ezer and R. Kosloff, *J. Chem. Phys.* **81**, 3967 (1984).
- ³⁶O. Koch and C. Lubich, *IMA J. Numer. Anal.* **31**, 379 (2011).
- ³⁷P.-O. Löwdin, *J. Math. Phys.* **3**, 1171 (1962).
- ³⁸L. S. Cederbaum, O. E. Alon, and A. I. Streltsov, *Phys. Rev. A* **73**, 043609 (2006).
- ³⁹See <http://www.dfg-spp1324.de> for DFG priority program 1324.