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ABSTRACT

By expressing the electronic wavefunction in an explicitly correlated (Jastrow-factorized) form, a similarity-transformed effective Hamiltonian can be derived. The effective Hamiltonian is non-Hermitian and contains three-body interactions. The resulting ground-state eigenvalue problem can be solved projectively using a stochastic configuration-interaction formalism. Our approach permits the use of highly flexible Jastrow functions, which we show to be effective in achieving extremely high accuracy, even with small basis sets. Results are presented for the total energies and ionization potentials of the first-row atoms, achieving accuracy within a mH of the basis-set limit, using modest basis sets and computational effort.

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Methods aiming to obtain high-accuracy solutions to the electronic Schrödinger equation must tackle two essential components of the problem, namely, providing highly flexible expansions capable of resolving nonanalytic features of the wavefunction, including the Kato cusps[1] at electron coalescence points, as well as treatment of many-electron correlation at medium and long range. The combination of these two facets of the problem leads to overwhelming computational complexity requiring large basis sets and high-order correlation methods, approximations to which can result in a significant loss of accuracy. The goal of achieving "chemical" accuracy remains extremely challenging for all but the simplest systems.

In Fock space approaches, including the majority of quantum chemical methodologies based on configurational expansions, the first-quantized Schrödinger Hamiltonian is replaced by a second-quantized form expressed in a one-electron basis. The passage from first quantization to the second is invoked primarily to impose antisymmetry on the solutions via fermionic creation and annihilation operators of the orbital basis. However, this formulation loses the ability to explicitly include *electron pair* variables (such as electron-electron distances) into the wavefunction, which has long been known[2] to be crucial in obtaining an efficient description of electron correlation. Correlation effects are then indirectly obtained via superpositions of Slater determinants over the Fock space, as in configuration interaction, coupled-cluster, and tensor-decomposition methods. These are computationally costly methods, especially with large basis sets. In quantum chemistry, explicitly correlated methods usually proceed via the R12 formalism of Kutzelnigg[3] and its more modern F12 variants[4] in combination with perturbation theory[5] or coupled-cluster theory.[6] These methods augment the Fock-space (configurational) wavefunctions with strongly orthogonal geminal terms with fixed amplitudes, imposing a first-order cusp condition. This approximation is suitable for systems whose ground state wavefunction is dominated by a single determinant. The inclusion of explicit correlation in strongly correlated, multideterminantal wavefunctions remains an open challenge.

In this paper, we postpone the passage to second quantization until after electron-pair information has been incorporated into the wavefunction. This is achieved by factorizing the electronic wavefunction Ψ in Jastrow[7] form,

$$\Psi = e^{\tau}\Phi, \tag{1}$$

where $\tau = \sum_{i<j} u(\mathbf{r}_i, \mathbf{r}_j)$ with $u(\mathbf{r}_i, \mathbf{r}_j) = u(\mathbf{r}_j, \mathbf{r}_i)$ is a symmetric correlation function over electron pairs and Φ is the associated many-body function we will aim to compute. The precise form of u has a significant bearing on the efficacy of the method[8–12] and will be later discussed. Substituting 1 into the Schrödinger equation $\hat{H}\Psi = E\Psi$ and rearranging, we obtain Φ as an eigenfunction of the similarity transformed (ST) Hamiltonian $\tilde{H}$, i.e., $\tilde{H}\Phi = E\Phi$, with

$$\tilde{H} = e^{-\tau}\hat{H}e^{\tau} = \hat{H} + [\hat{H}, \tau] + \frac{1}{2}[[\hat{H}, \tau], \tau]. \qquad (2)$$

The commutator expansion truncates at the second order because the only terms in $\hat{H}$ which do not commute with τ are the (second-derivative) kinetic energy operators. The explicit form of $\tilde{H}$ contains additional two- and three-body terms,

$$\tilde{H} = \hat{H} - \sum_i \left(\frac{1}{2}\nabla_i^2\tau + (\nabla_i\tau)\nabla_i + \frac{1}{2}(\nabla_i\tau)^2 \right)$$

$$= \hat{H} - \sum_{i<j}\hat{K}(\mathbf{r}_i, \mathbf{r}_j) - \sum_{i<j<k}\hat{L}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k),$$

where

$$\hat{K}(\mathbf{r}_i, \mathbf{r}_j) = \frac{1}{2}\Big(\nabla_i^2 u(\mathbf{r}_i, \mathbf{r}_j) + \nabla_j^2 u(\mathbf{r}_i, \mathbf{r}_j) + (\nabla_i u(\mathbf{r}_i, \mathbf{r}_j))^2$$

$$+ (\nabla_j u(\mathbf{r}_i, \mathbf{r}_j))^2 \Big) + (\nabla_i u(\mathbf{r}_i, \mathbf{r}_j) \cdot \nabla_i)$$

$$+ (\nabla_j u(\mathbf{r}_i, \mathbf{r}_j) \cdot \nabla_j),$$

$$\hat{L}(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \nabla_i u(\mathbf{r}_i, \mathbf{r}_j) \cdot \nabla_i u(\mathbf{r}_i, \mathbf{r}_k) + \nabla_j u(\mathbf{r}_j, \mathbf{r}_i) \cdot \nabla_j u(\mathbf{r}_j, \mathbf{r}_k)$$

$$+ \nabla_k u(\mathbf{r}_k, \mathbf{r}_i) \cdot \nabla_k u(\mathbf{r}_k, \mathbf{r}_j).$$

The similarity transformed Hamiltonian is non-Hermitian, owing to the gradient terms in $\hat{K}$. Projective techniques can be used to obtain the distinct right or left eigenvectors for a given eigenvalue E. The FCIQMC (full configuration interaction quantum Monte Carlo) method and its initiator approximation[13,14] has been previously adapted for this purpose[15,16] and we use it in this study. Note that our method differs from the Transcorrelated (TC) method of Boys and Handy[17] and modern extensions[18] in three crucial aspects: we solve for Φ as a full multideterminant expansion (to be obtained via an FCIQMC procedure) while Φ is a single Slater determinant in their work. Second, the formal unitary invariance of our Φ negates the need for orbital optimization and we simply use Hartree-Fock (HF) orbitals as the basis of our Fock space. Third, we do not attempt simultaneous optimization of the Jastrow function and Φ. Many of the difficulties associated with the non-Hermitian nature of $\tilde{H}$, which have plagued many previous attempts at the TC method, are thus avoided. The multideterminant nature of Φ also gives much greater flexibility to this function than a single Slater determinant, which we believe to be crucial in obtaining high accuracy. Indeed, Φ must share the same nodal surface as Ψ for an exact factorization, and a full CI form for Φ gives it much more flexibility in this regard than orbital optimization within a Slater-Jastrow form. This is a fundamental advantage of the present method, in addition to the avoidance of the often troublesome redundancy in the orbital optimization and Jastrow optimization procedure. Of course, the price to

be paid is a formally exponential scaling method. However, the cost of this can be ameliorated via the stochastic FCIQMC procedure. Our approach differs from that of the related work of Ten-no[19,20] in that we use a highly flexible form for both the Jastrow and multideterminantal expansions, rather than using a fixed short-ranged Jastrow function and a low order perturbative or coupled-cluster expansion.

Using this first-quantized Hamiltonian, we can construct a second-quantized Hamiltonian for a given set of orbitals $\{\phi_1, \ldots, \phi_M\}$ with the corresponding spin-$\frac{1}{2}$ creation (annihilation) operators $a_{p\sigma}^{\dagger}(a_{p\sigma})$,

$$\tilde{H} = \sum_{pq\sigma} h_q^p a_{p\sigma}^{\dagger} a_{q\sigma} + \frac{1}{2}\sum_{pqrs}(V_{rs}^{pq} - K_{rs}^{pq})\sum_{\sigma\tau} a_{p\sigma}^{\dagger} a_{q\tau}^{\dagger} a_{s\tau} a_{r\sigma}$$

$$- \frac{1}{6}\sum_{pqrstu} L_{stu}^{pqr}\sum_{\sigma\tau\lambda} a_{p\sigma}^{\dagger} a_{q\tau}^{\dagger} a_{r\lambda}^{\dagger} a_{u\lambda} a_{t\tau} a_{s\sigma}, \qquad (3)$$

where $h_q^p = \langle\phi_p|h|\phi_q\rangle$ and $V_{rs}^{pq} = \langle\phi_p\phi_q|r_{12}^{-1}|\phi_r\phi_s\rangle$ are the one- and two-body terms of the Schrödinger Hamiltonian, respectively, and $K_{rs}^{pq} = \langle\phi_p\phi_q|\hat{K}|\phi_r\phi_s\rangle$ and $L_{stu}^{pqr} = \langle\phi_p\phi_q\phi_r|\hat{L}|\phi_s\phi_t\phi_u\rangle$ are the corresponding terms arising from the similarity transformation. Note that the 3-body operator $\hat{L}$ is Hermitian, and for real orbitals, it has 48-fold symmetry, a useful feature in reducing the memory requirement to store these integrals. Nevertheless, storage of the 6-index integrals represents the major bottleneck of this methodology, limiting us at present to about 100 orbitals. This bottleneck can be alleviated using tensor-decomposition and fast on-the-fly evaluation of the integrals, which will be the subject of future work.

Although the form of this similarity transformed Hamiltonian has been known for a long time,[21] to the best of our knowledge it has never been treated in its full form until now. We retain all three-body terms, motivated in part by our recent study of the two-dimensional Hubbard model using Gutzwiller similarity transformations[16] in which we show that the 3-body terms do not incur a huge cost in the FCIQMC formalism, and their full treatment enables essentially exact results to be obtained. Furthermore, this study shows that the similarity transformations can help enormously in the study of strongly correlated systems, by significantly compactifying the right eigenvector of the ground state (which are generally highly multiconfigurational otherwise). This suggests that the present formalism may also help in treating strongly correlated *ab initio* Hamiltonians in a manner beyond that of *post hoc* explicitly correlated methodologies.[22]

The formulation requires the calculation of additional non-Hermitian two-electron matrix elements and Hermitian three-electron matrix elements. These are computed using numerical quadrature over the direct product of atom centered grids built from Treutler-Ahlrichs radial grids and Lebedev angular grids, obtained from the PySCF program.[23] The numerical summations factorize into a series of steps with $N_{grid}^2 N_{bas}^2$, $N_{grid} N_{bas}^4$, or $N_{grid} N_{bas}^6$ cost, each of which are highly parallelizable, and convergence of the integrals with the grid size is rapid. Further details are provided in the supplementary material. Our numerical approach makes possible use of arbitrary forms of Jastrow function and all integrals necessary to carry out the ST-FCIQMC calculations are readily available.

In the present study of the first-row atoms and cations, we investigated two correlation factors of the form used by Boys and Handy,[17]

$$u(\mathbf{r}_i, \mathbf{r}_j) = \sum_{mno}^{m+n+o\leq 6} c_{mno}(\bar{r}_i^m \bar{r}_j^n + \bar{r}_j^m \bar{r}_i^n)\bar{r}_{ij}^o, \quad \bar{r} = \frac{r}{1+r}.$$

This function has electron-electron (e-e), electron-nucleus (e-n), and e-e-n 3-body terms, which arise from $m = n = 0$, $o > 0$, and $m, n > 0$, $o = 0$, and $m, n, o > 0$ terms, respectively. In this form of correlation factor, the s-wave Kato cusp condition can be satisfied, but not the p-wave or higher,[24] and this feature ultimately determines the asymptotic rate of convergence to the basis set limit.[25] The parameters c_{mno} are taken from the variance-minimization variational Monte Carlo (VMC) study of the first-row atoms of Schmidt and Moskowitz.[26] In the first case (termed SM7), we used a form without the e-e-n terms, and in the second (termed SM17), we used the full form of the Jastrow factor with 17 terms, including the e-e-n terms. Comparison of the results for the two correlation factors gives insight into the role played by the additional terms in the Jastrow factor in the present methodology.

The ST-FCIQMC calculations were performed in standard valence correlation quantum chemical basis sets, cc-pVXZ, X = D, T, Q (with 14, 30, and 55 basis functions, respectively). The non-Hermitian nature of the Hamiltonian, together with 3-body interactions, has previously been treated in FCIQMC[15,16] and implemented in the NECI code[27] and was further adapted for the molecular Hamiltonian presented here.

The results of the ST-FCIQMC calculations for the total atomic energies are shown in Table I. Reference energies are taken from the experiment, corrected for relativistic effects as computed by Chakravorty et al.[28] The errors in the total energies for the three basis sets are plotted in Fig. 1. For comparison with quantum chemistry methods, we also report energies computed using the coupled cluster method CCSD(T)[29] and its explicitly correlated variant CCSD(T)-F12.[30] The former gives an indication of the severity of the
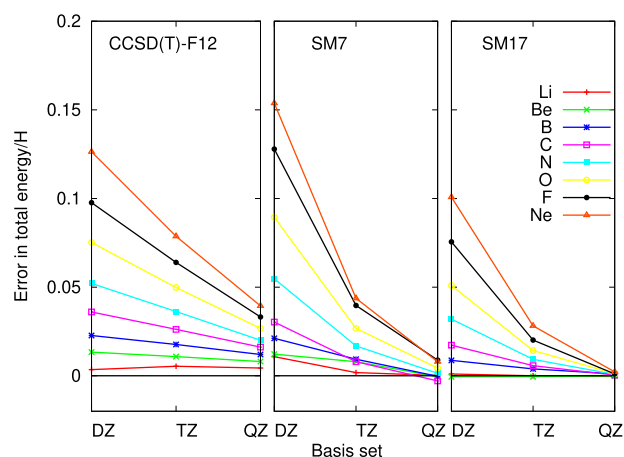

FIG. 1. Errors in the total energies of the atoms, in H, for the two correlation functions and the F12 methodology.

basis-set problem [for example, a mean absolute error (MAE) of 39 mH at cc-pVQZ], while the latter shows how much this error can be reduced using a state of the art explicit-correlation method when using valence basis sets for all-electron energies (MAE of 20 mH at cc-pVQZ). It is clear that the present methodology gives a marked improvement in the total energies, especially using the SM17 correlation factor: an MAE of only 1 mH with the cc-pVQZ basis set. A very small degree of nonvariationality (less than 1 mH) is observed in a few cases with the lighter elements. Strict variationality is lost in a non-Hermitian formulation and is often the major concern in transcorrelated methods, leading to energies far below the exact energy. Here, with the full treatment of the ST Hamiltonian, coupled with the projective eigensolver, the results show that this is of no serious concern. The cause of the present nonvariationality lies in the fact that the correlation factor does not fulfill the p-wave

TABLE I. Total atomic energies (hartrees), for CCSD(T), CCSD(T)-F12, and the ST Hamiltonian, using the SM7 and SM17 correlation factors. MAE for each method across the series is also shown.

Method	Basis	Li	Be	B	C	N	O	F	Ne	MAE
CCSD(T)	cc-pVDZ	−7.432 64	−14.617 41	−24.590 26	−37.761 56	−54.479 94	−74.911 155	−99.529 32	−128.680 69	0.121
	cc-pVTZ	−7.446 06	−14.623 79	−24.605 38	−37.789 53	−54.524 87	−74.984 94	−99.632 19	−128.815 13	0.069
	cc-pVQZ	−7.449 83	−14.640 08	−24.623 50	−37.812 09	−54.553 09	−75.023 19	−99.681 58	−128.876 76	0.039
F12	cc-pVDZ	−7.474 58	−14.654 00	−24.631 21	−37.809 01	−54.537 07	−74.992 08	−99.636 23	−128.811 25	0.053
	cc-pVTZ	−7.472 67	−14.656 53	−24.636 26	−37.818 83	−54.552 93	−75.017 52	−99.669 94	−128.858 90	0.036
	cc-pVQZ	−7.473 70	−14.659 33	−24.641 87	−37.828 84	−54.569 16	−75.040 56	−99.700 70	−128.898 16	0.020
SM7	cc-pVDZ	−7.467 26	−14.655 17	−24.632 79	−37.814 69	−54.534 48	−74.977 85	−99.606 02	−128.783 85	0.063
	cc-pVTZ	−7.476 27	−14.659 43	−24.644 58	−37.837 03	−54.572 36	−75.040 55	−99.694 21	−128.893 89	0.019
	cc-pVQZ	−7.477 85	−14.667 91	−24.654 17	−37.847 91	−54.587 78	−75.062 96	−99.725 07	−128.929 67	0.003
SM17	cc-pVDZ	−7.477 07	−14.667 93	−24.645 21	−37.827 72	−54.557 19	−75.016 39	−99.658 34	−128.836 82	0.036
	cc-pVTZ	−7.478 04	−14.667 89	−24.650 03	−37.839 28	−54.579 89	−75.053 03	−99.713 77	−128.909 44	0.010
	cc-pVQZ	−7.478 45	−14.667 49	−24.652 87	−37.844 61	−54.588 44	−75.066 09	−99.732 83	−128.935 42	0.001
Expt.		−7.478 06	−14.667 36	−24.653 91	−37.845 00	−54.589 20	−75.067 30	−99.733 90	−128.937 60	

TABLE II. IPs in mH, for the CCSD(T)-F12 method and for the ST Hamiltonian with the SM7 and SM17 correlation factors.

Method	Basis	Li	Be	B	C	N	O	F	Ne	MAE
F12	cc-pVDZ	197.70	341.36	302.47	410.24	529.60	490.44	629.71	780.26	6.07
	cc-pVTZ	197.67	341.81	304.13	412.73	532.91	496.17	636.44	789.34	2.39
	cc-pVQZ	197.82	341.98	304.53	413.52	534.21	498.77	639.20	792.62	0.96
SM7	cc-pVDZ	195.13	341.87	297.70	404.70	522.79	474.22	617.48	768.90	13.45
	cc-pVTZ	198.21	342.02	303.63	412.20	531.89	491.33	631.71	785.12	4.30
	cc-pVQZ	198.55	342.77	304.54	413.51	533.91	497.15	637.62	790.90	1.57
SM17	cc-pVDZ	188.50	341.40	299.54	407.46	526.84	482.62	627.60	779.22	9.65
	cc-pVTZ	198.54	342.64	305.66	414.66	535.31	499.05	640.95	793.95	0.58
	cc-pVQZ	198.44	342.70	304.98	414.24	535.19	500.65	642.37	795.82	0.50
Expt.		198.15	342.58	304.99	413.97	534.60	500.50	641.10	794.50	

cusp condition, leading to an over-correlation of the same-spin pairs of electrons, which prevents the accuracy reaching that is obtainable through F12 theory with high-order coupled cluster methods.[31] Spin-dependent correlation factors may be a way forward, but incur other complications, and is the subject of current work.

The additional 2- and 3-body terms turn out to make large but generally opposing changes to the total energies. For example, for the Ne atom in the cc-pVQZ basis, with the SM17 correlation factor the expectation values of these terms for the Hartree-Fock (HF) determinant are $\langle D_{HF}|\hat{K}|D_{HF}\rangle = -382$ mH and $\langle D_{HF}|L|D_{HF}\rangle = +109$ mH. The effect on the FCI energy is similar: the $\hat{K}$ terms reduce the energy below the exact energy (by 51 mH), while the L terms are substantially positive, making the total energy of $\bar{H}$ exact to within 2 mH. We also see that the SM17 correlation factor is much more effective than SM7. A key property of the SM17 form is that the correlation hole depth can vary depending on the distances of the pair of electrons from the nucleus, getting deeper if the pair is further away from the nucleus. This additional flexibility is very helpful in differentiating between the core-electron and valence-electron correlation.

We obtained the ionization potentials (IPs) by computing the cation total energies (Table II). Here, we used the same Jastrow parameters as used in the atomic calculations, without further optimization—this provides a stern test of the transferability of methodology. The results show that at both cc-pVTZ

and cc-pVQZ basis sets, the MAE for the IPs are only 0.58 and 0.50 mH for the SM17 correlation factor, compared to 2.39 and 0.96 for the CCSD(T)-F12 method. The marked improvement of the SM17 results over SM7 highlights the effectiveness of the e-e-n terms in the Jastrow functions to deliver very high accuracy even using the comparatively modest cc-pVTZ basis.

A promising aspect of the present approach is its ability to describe core electron correlation without the need to include tight functions in the basis-set, this already being evident in the excellent total energies of Table I. To investigate this further, in Table III, we report the series of the total energy of neon with differing numbers of electrons, from Ne to Ne^{7+}, which are increasingly dominated by the core electrons. The results from the ST-FCIQMC with the atomic SM17 Jastrow factor are particularly interesting as they give agreement in the total energy to within a couple of mH for all systems. This is without a core-correlation basis set. For the other methods such as CCSD(T)-F12, a core-valence basis set (e.g., cc-pCVQZ) is essential to describe the total energy. This, however, leads to a very significant increase in the size of the basis set (e.g., cc-pVQZ has 55, cc-pCVQZ 84, and cc-pCV5Z 145 basis functions). The ability of the present methodology to capture core correlation via the Jastrow factor, obviating the need to correlate them in the configurational expansion, is a major advantage that will prove even more useful in heavier systems.

TABLE III. Energies of the cations of Ne using SM17 vs CCSD(T) and CCSD(T)-F12.

Method	Basis	Ne^{7+}	Ne^{6+}	Ne^{5+}	Ne^{4+}	Ne^{3+}	Ne^{2+}	Ne^+	Ne
CCSD(T)	cc-pVQZ	−102.6530	−110.2577	−116.0512	−120.6884	−124.2615	−126.5857	−128.0871	−128.8768
CCSD(T)	cc-pV5Z	−102.6585	−110.2646	−116.0616	−120.7011	−124.2757	−126.6027	−128.1067	−128.8989
CCSD(T)	cc-pCVQZ	−102.6788	−110.2859	−116.0820	−120.7209	−124.2951	−126.6205	−128.1224	−128.9123
CCSD(T)	cc-pCV5Z	−102.6809	−110.2888	−116.0871	−120.7275	−124.3027	−126.6303	−128.1346	−128.9269
CCSD(T)-F12	cc-pCV5Z	−102.6818	−110.2900	−116.0891	−120.7303	−124.3062	−126.6359	−128.1420	−128.9360
ST-FCIQMC	cc-pVQZ	−102.6817	−110.2910	−116.0886	−120.7288	−124.3045	−126.6334	−128.1397	−128.9355
Expt.[28]		−102.6822	−110.2909	−116.0902	−120.7312	−124.3068	−126.6366	−128.1431	−128.9376

In conclusion, it is worthwhile reemphasizing a crucial difference between the present method and the standard explicitly correlated methods such as F12, namely, how the redundancy between the Jastrow function and the configurational function is dealt with. In the F12 methods, strong orthogonality projectors are used to eliminate this redundancy, i.e., correlation that can be described by the Fock space wavefunction (in a given basis set) is removed from the correlation factor. As such, only simple correlation functions, typically of the exponential form $u(\mathbf{r}_1, \mathbf{r}_2) = -\gamma^{-1} e^{-\gamma r_{12}}$, are employed in the F12 methods, more complicated forms (such as SM7 and SM17) being less effective because of the projections. In the present method, on the other hand, the configurational function Φ is explicitly solved *in the presence of the potential terms arising from the correlation function* and can benefit from them: a more realistic correlation function leads to a simpler Φ and more rapid convergence with respect to the parameters (basis set, CI expansion, etc.) that define Φ, hence the observed significant improvement in performance in going from SM7 to SM17.

To summarize, we show that eigenfunctions of a Jastrow-factorized similarity-transformed Hamiltonian can be computed using the FCIQMC technique and leads to accurate results for atoms, close to the basis-set limit, even when the configurational wavefunction is expanded in limited basis sets. A major advantage of the present approach, as compared to the F12 methodologies, is that forms of correlation factors beyond pure e-e functions can be used without the need for projection operators, and deliver excellent energies without the need for augmented basis sets. A further advantage, which comes from the FCI formulation presented, is the ability to tackle strongly correlated systems such as stretched open-shell molecules. This will be the subject of future work along with the optimization of Jastrow factors using different trial wavefunctions. The main bottleneck in the current implementation is the need to store 3-body integrals. Work is underway to alleviate this.

See the supplementary material for details of the numerical evaluation of the Hamiltonian matrix elements.

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