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Communication: ROHF theory made simple

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Restricted open-shell Hartree–Fock (ROHF) theory is formulated as a projected self-consistent unrestricted HF (UHF) model by mathematically constraining spin density eigenvalues. This constrained UHF (CUHF) wave function is identical to that obtained from Roothaan’s effective Fock operator. The α and β CUHF Fock operators are parameter-free and have eigenvalues (orbital energies) that are physically meaningful as in UHF, except for eliminating spin contamination. This new way of solving ROHF leads to orbitals that turn out to be identical to semicanonical orbitals. The present approach removes ambiguities in ROHF orbital energies. © 2010 American Institute of Physics. [doi:10.1063/1.3503173]

Restricted open-shell Hartree–Fock (ROHF) theory was formulated by Roothaan some 50 years ago.¹ A major drawback of this model is the lack of a unique effective Fock operator.² Even though the ROHF wave function and total energy obtained from different coupling schemes are the same, the resulting orbitals and orbital energies are different and lead to post-ROHF results that generally depend on them. The interpretation and physical picture emerging from Roothaan’s open-shell theory have always been somewhat blurry. Attempts to resolve these ambiguities, as well as many paradoxes resulting from them, are well documented in the literature.^{3–6}

On the other hand, the physical picture of unrestricted HF (UHF) is clear.⁷ It is a single-determinant wave function with well-defined α and β orbital energies obeying Koopmans’ theorem. It is straightforward to use it in post-UHF calculations by simply treating the α and β orbitals explicitly and separately. The notorious problem in UHF, however, is spin contamination: the wave function is not an eigenfunction of S^2 . This weakness is ubiquitous and a serious detriment when bonds are stretched. If the UHF wave function suffers from severe spin contamination, as is the case when strong static correlation is present, then UHF is no longer a good starting reference point for post-UHF treatments of correlation or excited states. Once lost, good quantum numbers are hard to recover, so when possible, it is preferable to use ROHF as a starting point despite the ambiguities regarding its associated Fock operator.

As a spin off of recent work on strong correlations,^{8,9} we have realized that the UHF energy can be written as a functional of the charge density matrix $\mathbf{P}=(\boldsymbol{\gamma}^\alpha+\boldsymbol{\gamma}^\beta)/2$ and the spin density matrix $\mathbf{M}=(\boldsymbol{\gamma}^\alpha-\boldsymbol{\gamma}^\beta)/2$, where $\boldsymbol{\gamma}^\alpha$ and $\boldsymbol{\gamma}^\beta$ are the α and β density matrices, respectively. This connection turns out to be enlightening for formulating ROHF as a constrained UHF (CUHF) theory. The resulting constrained UHF scheme here presented leads to well-defined α and β Fock operators with straightforward interpretation and no

spin contamination. The ROHF wave function, energy, charge, and spin densities remain the same; only the ROHF Fock operator is replaced by two UHF-like counterparts. As shown in benchmarks below, the meaning of the resulting orbitals and orbital energies is much more physical than in Roothaan’s approach and provide a base for treatments of electron correlation and excited states. At convergence of the iterative procedure, the orbitals resulting from our optimization procedure are the same as the semicanonical orbitals previously proposed in the literature.^{10–12} Our results give further justification to the use of these semicanonical orbitals.

Theory: The familiar energy expression in ROHF is

$$E_{\text{ROHF}} = 2 \sum_i f_i h_{ii} + \sum_{ij} f_i f_j (2a_i^j \langle ij|ij \rangle - b_i^j \langle ij|ji \rangle), \quad (1)$$

where h_{ij} are one-electron integrals, $\langle ij|kl \rangle$ are two-electron integrals in Dirac’s notation, a_i^j and b_i^j are the coupling coefficients, and f_i are the orbital occupations: 1 for core (doubly occupied, c) and 0 for virtual (unoccupied, v) orbitals. In the case of high-spin open-shell systems under consideration, $a = 1$, $b = 2$, and $f = 1/2$ for open-shell orbitals (singly occupied, o). Roothaan’s effective Fock operator is defined as

$$\mathbf{F}_{\text{ROHF}} = \begin{pmatrix} \mathbf{R}_{cc} & \mathbf{F}_{co}^\beta & \mathbf{F}_{cv}^{\text{cs}} \\ \mathbf{F}_{oc}^\beta & \mathbf{R}_{oo} & \mathbf{F}_{ov}^\alpha \\ \mathbf{F}_{vc}^{\text{cs}} & \mathbf{F}_{vo}^\alpha & \mathbf{R}_{vv} \end{pmatrix} \begin{matrix} \text{core}(c) \\ \text{open}(o) \\ \text{virtual}(v), \end{matrix} \quad (2)$$

where \mathbf{F}^α and \mathbf{F}^β are UHF α and β Fock matrices and $\mathbf{F}^{\text{cs}} = (\mathbf{F}^\alpha + \mathbf{F}^\beta)/2$. At self-consistent field (SCF) convergence, all off-diagonal \mathbf{F}_{ROHF} terms become zero. The choice of the diagonal elements in Eq. (2) is completely arbitrary within a set of A and B coupling parameters,

$$\mathbf{R}_{cc} = A_{cc} \mathbf{F}_{cc}^\alpha + B_{cc} \mathbf{F}_{cc}^\beta, \quad (3a)$$

$$\mathbf{R}_{oo} = A_{oo} \mathbf{F}_{oo}^\alpha + B_{oo} \mathbf{F}_{oo}^\beta, \quad (3b)$$

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The derivatives of E_{cs} with respect to γ^α and γ^β yield the usual closed-shell Fock matrix,

$$\frac{\partial E_{cs}}{\partial \gamma_{ij}^\alpha} = \frac{\partial E_{cs}}{\partial \gamma_{ij}^\beta} = \frac{1}{2} \frac{\partial E_{cs}}{\partial P_{ij}} \equiv F_{ij}^{cs}. \quad (14)$$

On the other hand, the derivatives of E_c are

$$-\frac{\partial E_c}{\partial \gamma_{ij}^\alpha} = \frac{\partial E_c}{\partial \gamma_{ij}^\beta} = \sum_{kl} \langle ik|lj \rangle M_{kl} \equiv \Delta_{ij}^{UHF}. \quad (15)$$

Hence,

$$\mathbf{F}^\alpha = \mathbf{F}^{cs} - \Delta^{UHF}, \quad (16a)$$

$$\mathbf{F}^\beta = \mathbf{F}^{cs} + \Delta^{UHF}, \quad (16b)$$

which are the usual UHF Fock matrices. Now, the CUHF Fock matrices additionally require the derivatives of the constraints in Eq. (12) with respect to γ^α and γ^β , which are trivially $\lambda_{ij}/2$ and $-\lambda_{ij}/2$, respectively. Defining Δ^{CUHF} as

$$\Delta_{ij}^{CUHF} \equiv \begin{cases} \Delta_{ij}^{UHF} - \frac{\lambda_{ij}}{2} & \text{if } \{i \in c \wedge j \in v\} \\ \Delta_{ij}^{UHF} & \text{or } \{i \in v \wedge j \in c\} \\ \Delta_{ij}^{UHF} & \text{otherwise} \end{cases} \quad (17)$$

yields the CUHF α and β Fock matrices,

$$\tilde{\mathbf{F}}^\alpha = \mathbf{F}^{cs} - \Delta^{CUHF}, \quad (18a)$$

$$\tilde{\mathbf{F}}^\beta = \mathbf{F}^{cs} + \Delta^{CUHF}. \quad (18b)$$

The CUHF equations to solve are $[\tilde{\mathbf{F}}^\alpha, \gamma^\alpha] = 0$ and $[\tilde{\mathbf{F}}^\beta, \gamma^\beta] = 0$. Subtracting these two SCF conditions and dividing it by 2 yields

$$\mathbf{F}^{cs} \mathbf{M} - \mathbf{M} \mathbf{F}^{cs} - \Delta^{CUHF} \mathbf{P} + \mathbf{P} \Delta^{CUHF} = 0. \quad (19)$$

Partitioning these matrices into core, open, and virtual blocks gives

$$\mathbf{F}_{co}^{cs} + \Delta_{co}^{CUHF} = \tilde{\mathbf{F}}_{co}^\beta = 0, \quad (20a)$$

$$\mathbf{F}_{vo}^{cs} - \Delta_{vo}^{CUHF} = \tilde{\mathbf{F}}_{vo}^\alpha = 0, \quad (20b)$$

$$\Delta_{cv}^{CUHF} = 0, \quad (20c)$$

where we have used $\mathbf{P}_{cc} = \mathbf{1}$, $\mathbf{P}_{vv} = \mathbf{P}_{cv} = \mathbf{P}_{co} = \mathbf{P}_{vo} = 0$, and $\mathbf{P}_{oo} = \mathbf{M}_{oo} = \frac{1}{2} \mathbf{1}$. Together with Eq. (17), Eq. (20c) implies that $\lambda_{cv} = 2\Delta_{cv}^{UHF}$ at convergence. During the iterative procedure, we choose this same value for λ_{cv} because it reduces δ_s at each SCF cycle. Note that Eqs. (20) yield the SCF conditions for Roothaan's ROHF. Finally, our CUHF α and β Fock matrices are

$$\tilde{\mathbf{F}}^\alpha = \begin{pmatrix} \mathbf{F}_{cc}^\alpha & \mathbf{F}_{co}^\alpha & \mathbf{F}_{cv}^{cs} \\ \mathbf{F}_{oc}^\alpha & \mathbf{F}_{oo}^\alpha & \mathbf{F}_{ov}^\alpha \\ \mathbf{F}_{vc}^{cs} & \mathbf{F}_{vo}^\alpha & \mathbf{F}_{vv}^\alpha \end{pmatrix} \quad \tilde{\mathbf{F}}^\beta = \begin{pmatrix} \mathbf{F}_{cc}^\beta & \mathbf{F}_{co}^\beta & \mathbf{F}_{cv}^{cs} \\ \mathbf{F}_{oc}^\beta & \mathbf{F}_{oo}^\beta & \mathbf{F}_{ov}^\beta \\ \mathbf{F}_{vc}^{cs} & \mathbf{F}_{vo}^\beta & \mathbf{F}_{vv}^\beta \end{pmatrix}. \quad (21)$$

These CUHF Fock matrices are different from the UHF ones only in the cv and vc blocks and are different from Roothaan's effective Fock matrix of Eq. (2). Our CUHF procedure yielding ROHF is surprisingly straightforward: one

TABLE I. Mean and mean absolute errors of ionization potentials ($-\varepsilon_{\text{HOMO}}$ in eV) of 24 open-shell systems (Ref. 20).

	ROHF			
	MD	PGB	CUHF	UHF
ME	-7.38	0.57	0.54	0.68
MAE	7.38	0.64	0.61	0.71

simply performs UHF with Fock matrices replaced by Eqs. (21). These Fock matrices eliminate ambiguities arising in ROHF theory and produce a more physical UHF-like picture. In open-shell molecules, α and β electrons feel different potentials; our $\tilde{\mathbf{F}}^\alpha$ and $\tilde{\mathbf{F}}^\beta$ operators are different from each other and yield α orbitals different from β orbitals that are true "canonical orbitals" obtained by diagonalization. However, unlike UHF, they have no spin contamination, which is removed by Lagrangian constraints. Their eigenvalues ε_i^σ are physical orbital energies in the sense that they are associated with individual α and β orbitals, satisfy Koopmans' theorem, and the aufbau principle,¹⁸ as opposed to many ROHF canonicalizations of Eq. (2).⁶ As mentioned above, the CUHF orbitals have previously been proposed in the literature as semicanonical orbitals for MP2.^{11,12} Our present work shows that the Fock matrices for which these orbitals are eigenfunctions appear naturally from a constrained UHF optimization that eliminates spin contamination.

Results: We have implemented CUHF in the Gaussian suite of programs¹⁹ and verified that our procedure converges to the ROHF energy. Unlike many ROHF schemes, CUHF presented no issues with SCF convergence in a large set of benchmark cases.²⁰ This is undoubtedly related to the observance of the aufbau principle in our method. Since Koopmans' theorem is valid for CUHF,¹² orbital energies approximate ionization potentials (IPs) and electron affinities. In Table I we summarize the mean (ME) and mean absolute errors (MAE) of first IPs estimated via highest occupied molecular orbital (HOMO) energies ($\varepsilon_{\text{HOMO}}$) for 24 open-shell compounds selected from the G2 set.²¹ Molecular geometries are optimized with B3LYP/6-31G(2df,p). CUHF results with a 6-311++G(3df,3pd) basis are compared to UHF and the default ROHF implementation in Gaussian (parameters of McWeeny and Diercksen,²² denoted as MD). In all systems, the CUHF $\varepsilon_{\text{HOMO}}$ captures the right physics yielding IPs comparable to those of UHF yet preserving the correct $\langle S^2 \rangle$ expectation value.

We have compared our CUHF orbital energies with those obtained by Eq. (2) with parameters recently suggested by Plakhutin *et al.*² and Davidson and Plakhutin.⁵ These parametrizations are chosen to obey Koopmans' theorem. However, both schemes usually yield poor SCF convergence.²⁰ Therefore, as a simple remedy to obtain Plakhutin–Gorelik–Breslavskaya (PGB) and Davidson–Plakhutin (DP) results in this paper, we have used the converged ROHF wave function and then diagonalized Eq. (2) with PGB and DP parameters in a single shot. The eigenvalues thus obtained are identical to those from the self-consistent PGB and DP schemes. For most systems, CUHF gives first IPs very similar to PGB.²⁰ In

TABLE II. Orbital energies of $\text{MnCl}_2(\text{H}_2\text{O})_2$ (in eV).

MO	PGB+DP		CUHF	
	α	β	α	β
b_2	-11.310	-11.079	-10.807	-11.079
a_2	-11.415	-11.159	-10.909	-11.159
a_1	-11.362	-11.168	-10.910	-11.168
b_1	-11.327	-11.162	-11.195	-11.162
b_2	-12.083	-11.676	-11.741	-11.676
a_1	-13.112	-12.405	-11.684	-12.405
$3d_{x^2-y^2}^{\text{Mn}}$	-15.748		-15.742	
b_1	-16.470	-16.319	-16.635	-16.319
$3d_{yz}^{\text{Mn}}$	-16.552		-17.262	
a_1	-16.613	-16.417	-17.728	-16.417
$3d_{xz}^{\text{Mn}}$	-16.658		-15.811	
$3d_{xy}^{\text{Mn}}$	-16.701		-17.129	
$3d_{z^2}^{\text{Mn}}$	-16.924		-17.095	
a_1	-18.942	-18.665	-19.257	-18.665

Table II, we present valence orbital energies for a model high spin transition metal complex $\text{MnCl}_2(\text{H}_2\text{O})_2$ in C_{2v} symmetry. This is an example where ionization from closed shells is easier than ionization from ROHF open-shells.²³ CUHF poses no convergence problems²⁰ and the orbital energies are in fair agreement with those of PGB and DP. Additional data for O_2 and NO_2 are presented in the Supplementary Material.²⁰

Last, we present excitation energies of five small open-shell molecules calculated with time-dependent HF (TDHF) based on UHF and CUHF with a 6-311++G(3df,3pd) basis. The bond-lengths for BeF and CO^+ (not included in the G2 set) are 1.355 and 1.078 Å, respectively. For TD-CUHF, we have used CUHF orbitals and orbital energies in the TD-UHF procedure. Although this TD-CUHF scheme is not rigorous (one should calculate the linear response of $\tilde{\mathbf{F}}$ instead of \mathbf{F}), this simple approximation turns out to be quite reasonable as shown in Table III. When UHF spin contamination (δ_s) is small, TD-UHF and TD-CUHF give very similar results. As δ_s becomes larger, however, TD-UHF greatly overestimates the excitation energies. On the other hand, by retaining a spin projected reference ($\delta_s=0$), TD-CUHF gives more reasonable excitation energies outperforming TD-UHF in spin contaminated situations.

In closing, we would like to make clear that the optimum method for solving ROHF is unrelated to how the orbitals will be used. The convergence method should be optimized and then the orbitals can be transformed in many ways for different purposes.

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TABLE III. TDHF valence (V) and Rydberg (R) excitation energies (in eV) of open-shell molecules. Numbers in parentheses are UHF spin contamination δ_s .

System	State	CUHF	UHF	Exptl. ^a
BeF (0.001)	V $^2\Pi$	4.19	4.20	4.14
	R $^2\Sigma^+$	6.33	6.34	6.16
	R $^2\Sigma^+$	6.54	6.54	6.27
BeH (0.002)	V $^2\Pi$	2.64	2.69	2.48
	R $^2\Pi$	6.25	6.26	6.32
CH ₃ (0.012)	R $^2A'_1$	6.23	6.54	5.73
	R $^2A''_2$	7.34	7.73	7.44
CO ⁺ (0.141)	V $^2\Pi$	4.84	6.93	3.26
	V $^2\Sigma^+$	9.81	11.10	5.82
CN (0.397)	V $^2\Pi$	0.85	4.11	1.32
	V $^2\Sigma^+$	1.62	5.41	3.22
ME		0.41	1.43	
MAE		0.81	1.44	

^aTaken from Ref. 24.

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