

Optimized effective potential from a correlated wave function: OEP-GVB

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Abstract

The optimized effective potential (OEP) method allows orbital-dependent functionals to be used in density functional theory (DFT). Traditionally the orbital-dependent functional of interest has been the Hartree-Fock energy, leading to exact exchange (OEP-HF or EXX) density functional theory. Here we present results that use a generalized valence-bond (GVB) wave function, a multi-configurational wave function that includes static correlation and dissociates to the proper limits. We demonstrate the effectiveness of the OEP-GVB method by showing the dissociation of H_2 and the excitation spectrum of He.

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I. INTRODUCTION

The optimized effective potential (OEP) method [1] is a technique for obtaining density functionals from orbital-dependent energy functions. Along with the closely-related exact exchange (EXX) method of Görling and coworkers [2–5], these methods have allowed the generation of exchange functionals that derive from the HF exchange energy expression and yet are true density functionals. For the purposes of the current discussion, we will refer to OEP methods that use HF as the orbital-dependent objective energy functional as OEP-HF. The inclusion of exact exchange has allowed more accurate computation of properties such as band gaps and the excited-state spectrum [5–10].

The purpose of the current work is to explore appropriate correlation functionals to accompany the exchange functional produced by OEP-HF approaches. There have already been many attempts along these lines. Several investigators have included LDA or GGA correlation functionals [9]. There have been several attempts based on perturbation theory, most notably Bartlett and coworkers [6, 11], who have introduced the OEP-MBPT2 method that is based upon a second-order many-body perturbational correction to the Hartree-Fock energy.

The current work introduces an approach based on a *variational* description of the electron correlation. We take as our orbital-dependent functional a generalized valence bond perfect-pairing (GVB-PP) wave function [12], a multi-configurational wave function that contains static electron correlation and dissociates to the proper limits. In contrast to most multi-configurational self-consistent field (MC-SCF) approaches, GVB-PP does not require a full four-index transformation of the two-electron integrals, and, as such, scales roughly the same as HF or DFT calculations with problem size. The resulting approach, OEP-GVB, provides a computationally tractible density functional theory method containing exact exchange and static correlation. We demonstrate the effectiveness of OEP-GVB by showing dissociating H_2 and the excitation spectrum of He.

II. METHODS

A. Optimized Effective Potential

In the OEP method one writes the KS equations in the form of a kinetic energy operator t , a nuclear attraction potential $v_N(r)$, and an optimized effective potential $v_{OEP}(r)$:

$$[t + v_N(r) + v_{OEP}(r)]\phi_i = \epsilon_i\phi_i. \quad (1)$$

The OEP potential $v_{OEP}(r)$ is determined by minimizing an orbital dependent objective energy function $E[\{\phi_i\}]$. We follow Yang and Wu [13], who define a particularly elegant technique whereby the OEP is expanded in a set of Gaussian functions $g(r)$ about a reference potential $v_0(r)$

$$v_{OEP}(r) = v_0(r) + \sum_{\ell} b_{\ell}g_{\ell}(r). \quad (2)$$

Yang and Wu take the reference potential $v_0(r)$ to be the Fermi-Amaldi potential

$$v_0(r) = \frac{N-1}{N} \int \frac{\rho_0(r')}{|r-r'|} dr'. \quad (3)$$

Because the reference potential is independent of v_{OEP} , the derivative may be obtained by minimizing the energy functional with respect to the expansion coefficients b_{ℓ} via

$$\begin{aligned} \frac{\delta E[\{\phi_i\}]}{\delta v_{OEP}} &= \sum_{\ell} \frac{\delta E[\{\phi_i\}]}{\delta b_{\ell}} \\ &= \sum_{\ell} \sum_{i,j \neq i} \int \frac{\delta E[\{\phi_i\}]}{\delta \phi_i(r)} \phi_j(r) dr \frac{\langle \phi_j | g_{\ell} | \phi_i \rangle}{\epsilon_i - \epsilon_j} \end{aligned} \quad (4)$$

The orbital-dependent energy functional $E[\{\phi_i\}]$ is typically taken to be the Hartree-Fock energy, although it can in fact be any orbital-dependent functional. The following section will describe the GVB-PP approach, which we shall use as the orbital-dependent energy function to optimize.

B. GVB and OEP-GVB

The HF wave function contains only a single electronic configuration: in the HF description of H_2 both electrons occupy the bonding orbital ϕ_g , shown in Figure 1, and in the HF description of He both electrons occupy the orbital ϕ_{1s} , shown in Figure 2. This single

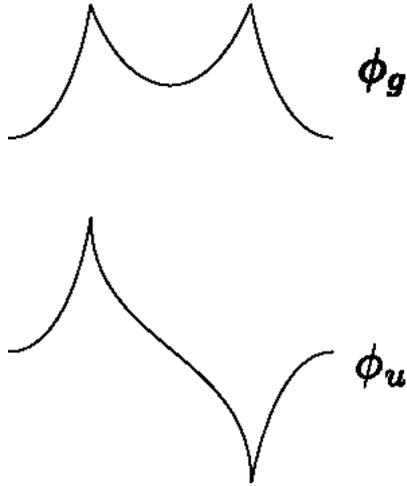


FIG. 1: The first and second natural orbitals for H_2 .

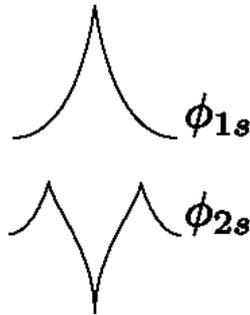


FIG. 2: The first and second natural orbitals for He.

configuration limits the ways the wave function can be variationally minimized and leads to, for example, the well-known problem of the HF description of H_2 dissociating to the wrong limits, shown in Figure 3. Although it is possible to properly describe the dissociation of H_2 using an unrestricted HF (UHF) description, the resulting wave function contains spin contamination and is thus no longer an eigenfunction of the spin S^2 operator.

The GVB-PP wave function [12] adds a variationally determined amount of another electronic configuration that gives the overall wave function greater freedom. In H_2 , the GVB-PP wave functions adds the antibonding orbital ϕ_u , shown in Figure 1, which allows the two electrons to build in some static electron correlation and to dissociate properly, shown in Figure 3. In He, the GVB-PP wave function adds the second atomic orbital ϕ_{2s} , shown in Figure 2, which allows the two electrons to build in some static electron correlation

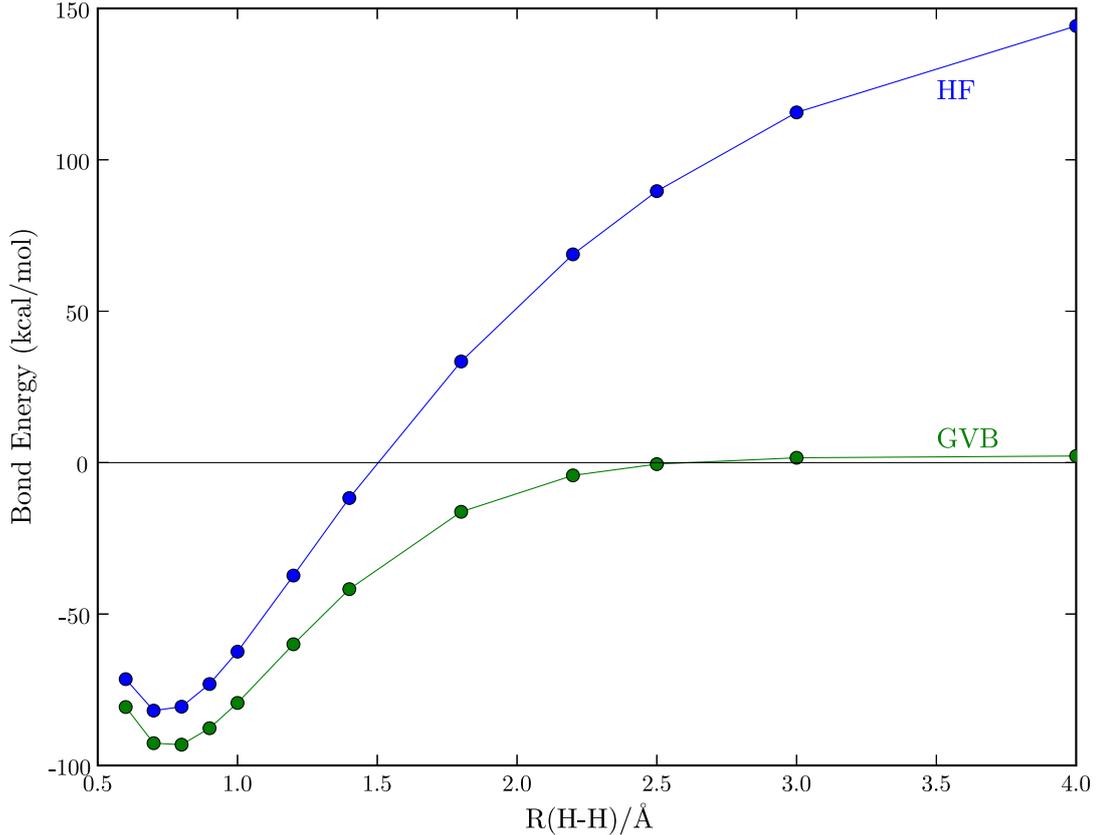


FIG. 3: A comparison of the bond energy (kcal/mol) of H_2 during dissociation using the one-configuration HF wave function (blue circles) and the two-configuration GVB-PP wave function (green circles). Only the GVB wave function dissociates to the correct limit.

and avoid each other to some degree. In the GVB terminology, the orbitals ϕ_g and ϕ_u , or ϕ_{1s} and ϕ_{2s} , are the first and second *natural orbitals* of a *GVB pair*.

For two electron systems with one GVB pair, the GVB-PP wave function takes a particularly simple form. For the purposes of our discussion, we will refer to the first and second natural orbitals of the GVB pair as ϕ_a and ϕ_b .

$$\Psi_{GVB} = (c_a\phi_a^2 - c_b\phi_b^2)\alpha\beta. \quad (5)$$

ϕ_a and ϕ_b are spatial orbitals, and α and β are the corresponding spin components. The coefficients c_a and c_b are determined by solving the 2×2 configuration interaction (CI) matrix:

$$\mathbf{HC} = \mathbf{\Lambda C} \quad (6)$$

where

$$\mathbf{H} = \begin{pmatrix} E_a & K_{ab} \\ K_{ab} & E_b \end{pmatrix}. \quad (7)$$

The CI matrix elements are given by

$$E_a = 2h_{aa} + (aa|aa) \quad (8)$$

$$E_b = 2h_{bb} + (bb|bb) \quad (9)$$

$$K_{ab} = (ab|ab) \quad (10)$$

The one-electron terms h_{ij} are given by

$$h_{ij} = \int \phi_i(r)h(r)\phi_j(r)dr \quad (11)$$

and h contains the kinetic-energy and nuclear attraction terms. The two-electron terms $(ij|kl)$ are in *chemist's notation* (see, for example, reference [14]) and are given by

$$(ij|kl) = \int \frac{\phi_i^*(r_1)\phi_j(r_1)\phi_k^*(r_2)\phi_l(r_2)}{|r_1 - r_2|} d^3r_1 d^3r_2. \quad (12)$$

After the CI coefficients are determined, the GVB-PP energy may be determined as

$$E_{GVB} = c_a^2 E_a + c_b^2 E_b + 2c_a c_b K_{ab} + E_{ZZ'} \quad (13)$$

where $E_{ZZ'}$ is the nuclear repulsion energy.

In the current work we take eq (13) to be the objective function to be optimized via eq (4). The derivatives $\delta E_{GVB}/\delta b_\ell$ are straightforward given the relations

$$\int \frac{\delta E_{GVB}}{\delta \phi_a(r)} \phi_j(r) dr = c_a^2 (h_{aj} + (aa|aj)) + c_b c_a (ba|bj), \quad (14)$$

$$\int \frac{\delta E_{GVB}}{\delta \phi_b(r)} \phi_j(r) dr = c_b^2 (h_{bj} + (bb|bj)) + c_b c_a (ba|ja). \quad (15)$$

C. Basis Sets

For the H₂ results presented in this work, we use a 6-31G** contracted Gaussian basis set; the final basis set for H₂ has 10 contracted Gaussian basis functions. The He excited states required a much more elaborate basis set to converge their energies. We start with an aug-cc-pVTZ basis set and add 4 additional *spd* shells (a total of 5 diffuse shells, including the aug *spd* functions), the exponents of each one scaled a factor of 3. The final basis set has 65 contracted Gaussian basis functions, and is shown in Table I.

TABLE I: Contracted Gaussian basis sets used for He calculations in this paper. Our basis is a cc-pVTZ basis set, with 5 diffuse s -, p -, and d -shells added to converge the various excited states

Valence			Diffuse		
Type	Exponent	Coefficient	Type	Exponent	Coefficient
S	234.000000	0.002587	S	0.051380	1.000000
	35.160000	0.019533	P	0.199300	1.000000
	7.989000	0.090998	D	0.459200	1.000000
	2.212000	0.272050	S	0.017127	1.000000
S	0.666900	1.000000	P	0.066433	1.000000
S	0.208900	1.000000	D	0.153067	1.000000
P	3.044000	1.000000	S	0.005709	1.000000
P	0.758000	1.000000	P	0.022144	1.000000
D	1.965000	1.000000	D	0.051022	1.000000
			S	0.001903	1.000000
			P	0.007381	1.000000
			D	0.017007	1.000000
			S	0.000634	1.000000
			P	0.002460	1.000000
			D	0.005669	1.000000

D. Other Computational Details

For the GVB-PP description of H_2 we use the GAMESS program suite [15]. The B3LYP, BLYP and PBE results were obtained using the Jaguar program suite [16].

III. RESULTS

A. Dissociation of H_2

Table II shows energies (Hartree atomic units) for H_2 as the H—H distance (\AA) is increased. For H_2 , the OEP-HF results are identical to the HF results, and thus exhibits

TABLE II: Comparison of HF, GVB, OEP-GVB, BLYP and B3LYP bond energies (in Hartree atomic units) versus H—H (in Å) for H₂ dissociation. OEP-HF gives the same results as HF.

R/Å	HF	GVB	OEP-GVB	BLYP	B3LYP
0.6	-1.1139	-1.1286	-1.1256	-1.1479	-1.1593
0.7	-1.1305	-1.1476	-1.1441	-1.1663	-1.1772
0.8	-1.1284	-1.1484	-1.1447	-1.1663	-1.1766
0.9	-1.1165	-1.1398	-1.1359	-1.1566	-1.1663
1.0	-1.0995	-1.1265	-1.1226	-1.1421	-1.1510
1.2	-1.0594	-1.0956	-1.0915	-1.1079	-1.1151
1.4	-1.0186	-1.0666	-1.0626	-1.0739	-1.0793
1.8	-0.9468	-1.0259	-1.0241	-1.0181	-1.0194
2.2	-0.8904	-1.0067	-1.0061	-0.9795	-0.9765
2.5	-0.8571	-1.0008	-1.0007	-0.9597	-0.9536
3.0	-0.8157	-0.9975	-0.9974	-0.9387	-0.9282
4.0	-0.7702	-0.9965	-0.9965	-0.9214	-0.9051

the same difficulties dissociating that the HF wave function does. BLYP and B3LYP also dissociate to the incorrect limit, although closer to the correct result than the HF or OEP-HF results. The GVB and OEP-GVB methods dissociate to nearly the correct limit (the error shown here is predominantly due to finite basis set size effects). The GVB and OEP-GVB methods do not yield exactly the same energies because the orbitals in the OEP-GVB method are slightly constrained by the requirement that they come from a Kohn-Sham equation of the form of eq (1). This is similar to the energy differences seen between the HF and OEP-HF method (for example, in reference [13]), and was explained particularly well by Kummel and Perdew in reference [17]. These data are shown graphically in Figure 4.

It is, of course, possible to dissociate a chemical bond using a unrestricted HF or a spin-polarized DFT approach. However, these approaches only dissociate the bond properly because they introduce spin contamination into the wave functions, making the wave functions no longer eigenfunctions of S^2 , and the energies somewhat suspect. We believe that the performance of OEP-GVB in this capacity, coupled with the excitation spectrum

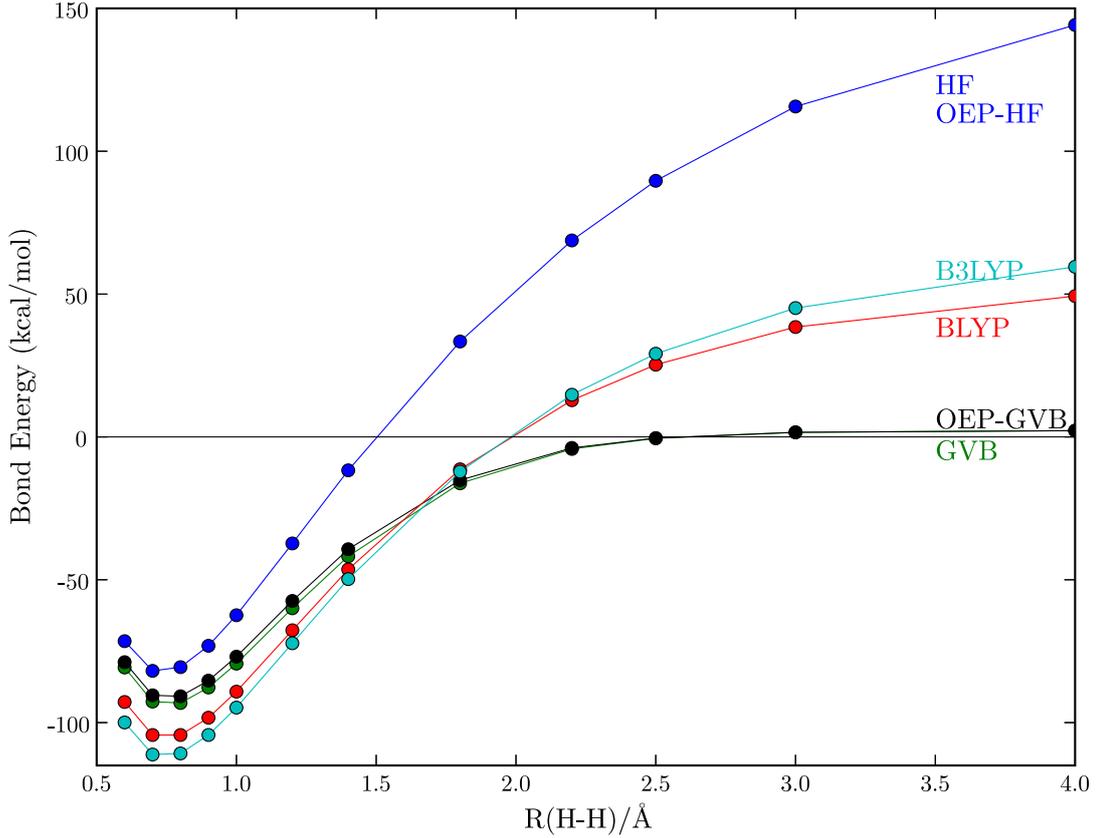


FIG. 4: Comparison of HF (blue circles), GVB (green circles), OEP-GVB (black circles), BLYP (red circles) and B3LYP (cyan circles) bond energies (kcal/mol) versus H—H (in Å) for H_2 dissociation. Here OEP-HF gives the same results as HF. Only the GVB and OEP-GVB methods dissociate to the proper limits.

discussed below, argue strongly for the current method.

B. The excitation spectrum of He

In KS DFT, only the highest occupied eigenvalue has a true physical interpretation, corresponding to the negative of the lowest ionization energy. In reference [19], Savin, Umrigar and Gonze derive a nearly exact Kohn-Sham potential from quantum Monte Carlo (QMC) calculations, and demonstrate that the resulting KS eigenvalues reproduce values from experiment [18] and explicit Hylleraas coordinate calculations of the excited states [20, 21]. The experiments and Hylleraas calculations give different values for the singlet and triplet excited states; in contrast, the KS eigenvalues from the QMC exchange-correlation

TABLE III: Comparison of the Helium experimental excited state spectrum to experimental values (reference [18]) and those resulting from differences in eigenvalues using a high-quality QMC-derived exchange-correlation functional (reference [19]), and those from HF, LDA, BLYP, PBE, B3LYP, and our OEP-HF and OEP-GVB approaches. The final row reports the mean absolute deviation (MAD) between the QMC-derived exchange-correlation functional and the other techniques.

State	Experiment		QMC	OEP						
	Triplet	Singlet		HF	LDA	BLYP	PBE	B3LYP	HF	GVB
1s→2s	0.728	0.758	0.746	0.918	0.571	0.585	0.580	0.662	0.762	0.760
1s→2p	0.770	0.780	0.777	0.923	0.576	0.590	0.585	0.667	0.793	0.790
1s→3s	0.835	0.842	0.839	0.922	0.574	0.587	0.582	0.665	0.856	0.853
1s→3p	0.846	0.848	0.848	0.941	0.592	0.605	0.600	0.683	0.864	0.862
1s→3d	0.848	0.848	0.848	0.936	0.589	0.603	0.598	0.680	0.865	0.862
1s→4s	0.867	0.870	0.869	0.929	0.580	0.594	0.591	0.673	0.885	0.882
MAD				0.107	0.241	0.227	0.232	0.160	0.016	0.014

functional yield only a single, spin-averaged value for each state. The fact that these values fall between the singlet and triplet energies for each state is a remarkable result, which the authors interpret as evidence that the Kohn-Sham orbitals arising from their QMC-based Kohn-Sham potential and the exact quasiparticle orbitals obey the same long-range equations to order $1/r^4$. For the remainder of this paper we will take the KS eigenvalues from reference [19] to be the “correct” values.

In the current work we report excitation spectra for He using OEP-HF and OEP-GVB. Although these results do not display the same quantitative agreement with experiment and Hylleraas calculations that those in reference [19] do, these methods come with substantially less computational expense. The accuracy of these results demonstrates that this approach does, in fact, exhibit the correct long-range behavior, and provides hope that inexpensive DFT calculations might yield the quantitative accuracy that Savin, Umrigar, and Gonze’s QMC-based KS-DFT calculations provided.

Table III reports a comparison of Helium excitation energies to the QMC-derived exchange-correlation functional as well as to HF and to other LDA and GGA functionals. We report the mean absolute deviation (MAD) between the QMC-derived values and

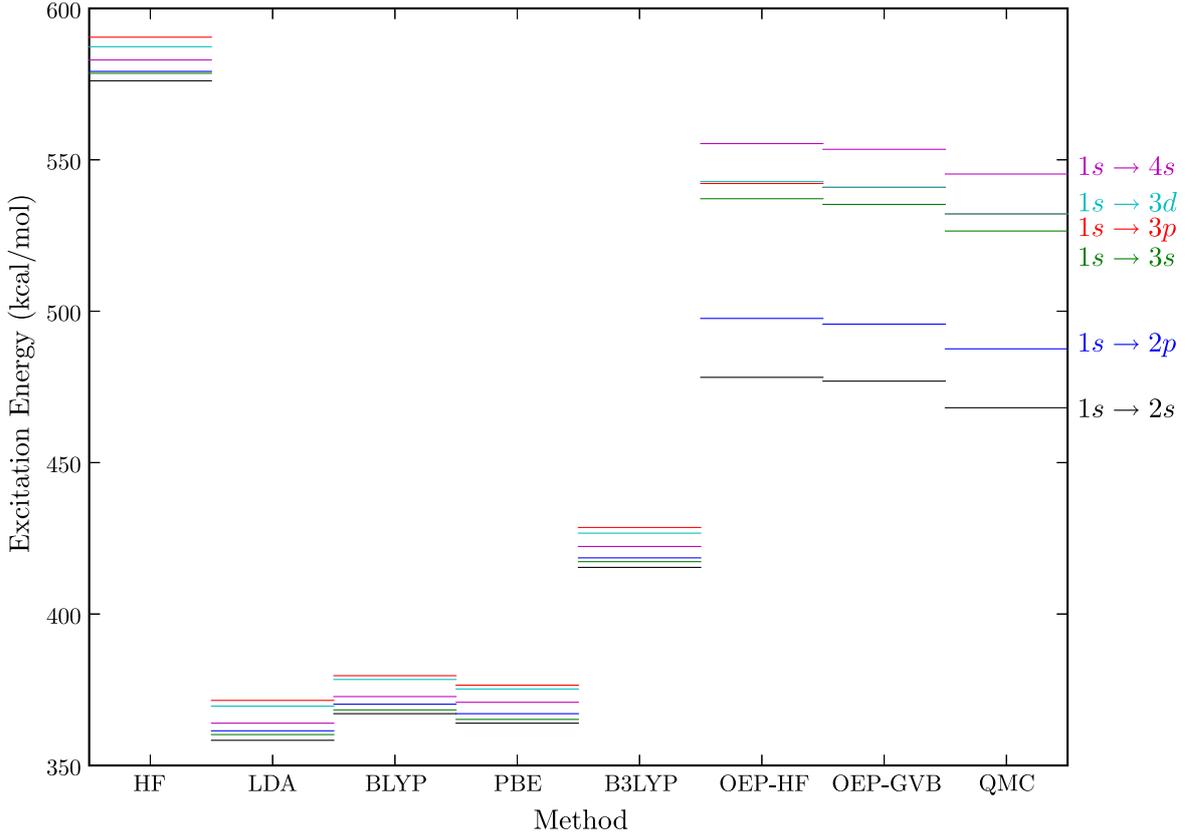


FIG. 5: Comparison of excitation energies for He atom computed from the KS-DFT eigenvalues using HF, LDA, BLYP, PBE, OEP-HF, OEP-GVB, and QMC exchange-correlation functionals. The levels are color-coded based on the excitation, shown at the right. The OEP methods are the only ones that obtain the correct ordering of the states, and the errors are reasonably constant across the whole spectrum, in contrast with the other approaches.

those from HF and the DFTs. The HF excitation energies differ on the average by 0.107 h, the LDA, BLYP, and PBE values differ by 0.241–0.273 h, and the B3LYP method by 0.160 h. The exchange-only OEP-HF values differ by only 0.016 h, and those using OEP-GVB improve upon that slightly, differing by 0.014 h. Moreover, the OEP values differ from the QMC values by essentially constant values across their entire spectra, whereas the LDA, GGA, hybrid, and HF values fluctuate much more about their average deviation. As a result, the OEP methods are the only methods that get the ordering of the states correct. These spectra are shown graphically in Figure 5.

IV. CONCLUSION

We have introduced the OEP-GVB DFT method that combines an exact-exchange technique with a static description of the electron correlation. The OEP-GVB method has the same computational expense as a HF or DFT program, which means that this method can be used for accurate description of large molecules at modest computational expense. We demonstrate the OEP-GVB dissociates the chemical bond in H_2 to the proper limits. We also demonstrate that the OEP-GVB method makes small improvements upon the OEP-HF calculation of the excitation spectrum of He. As proper bond dissociation and the proper band gap descriptions are two of the more important issues motivating the development of new DFT functionals, we believe that OEP-GVB can play an important role in this arena.

V. ACKNOWLEDGEMENT

The calculations in this paper were computed using the author's PyQuante program, which is available under a BSD license from <http://pyquante.sourceforge.net>; we anticipate releasing the OEP module shortly. We would like to thank Bill Camp for suggesting this approach for an orbital-dependent correlation functional, Daniel Rohr for helpful discussions on OEP, and John Aidun, Peter Schultz and Cyrus Umrigar for helpful comments on this manuscript. We would also like to thank Schrodinger, Inc., for providing a copy of the Jaguar program suite. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

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- [1] J. D. Talman and W. F. Shadwick. Optimized effective atomic central potential. *Physical Review A*, 14:36, 1976.
 - [2] Andreas Görling and Mel Levy. Correlation-energy functional and its high-density limit obtained from a coupling-constant perturbation expansion. *Physical Review B*, 47:13105, 1993.
 - [3] Andreas Görling and Mel Levy. Exact Kohn-Sham scheme based on perturbation theory. *Physical Review A*, 54:196, 1994.

- [4] Andreas Görling. Exact treatment of exchange in Kohn-Sham band-structure schemes. *Physical Review B*, 53:7024, 1996.
- [5] Martin Stadele, J. A. Majewski, P. Vogl, and Andreas Görling. Exact Kohn-Sham exchange potential in semiconductors. *Physical Review Letters*, 79:2089, 1997.
- [6] Ireneusz Grabowski, So Hirata, Stanislav Ivanov, and Rodney J. Bartlett. Ab initio density functional theory: OEP-MBPT(2). a new orbital-dependent correlation functional. *Journal of Chemical Physics*, 116:4415, 2002.
- [7] Martin Stadele, J. A. Majewski, P. Vogl, and Andreas Görling. Exact exchange Kohn-Sham formalism applied to semiconductors. *Physical Review Letters*, 79:2089, 1997.
- [8] Martin Stadele and Richard M. Martin. Metallization of molecular hydrogen: Predictions from exact-exchange calculations. *Physical Review Letters*, 84:6070, 2000.
- [9] R. J. Magyar, A. Fleszar, and E. K. U. Gross. Exact-exchange density-functional calculations for noble-gas solids. *Physical Review B*, 69:45111, 2004.
- [10] So Hirata, Stanislav Ivanov, Rodney J. Bartlett, and Ireneusz Grabowski. Exact-exchange time-dependent density-functional theory for static and dynamic polarizabilities. *Physical Review A*, 71:032507, 2005.
- [11] Rodney J. Bartlett, Victor F. Lotrich, and Igor V. Schweigert. Ab initio density functional theory: The best of both worlds? *Journal of Chemical Physics*, 123:62205, 2005.
- [12] Frank W. Bobrowicz and William A. Goddard, III. The self-consistent field equations for generalized valence bond and open-shell Hartree-Fock wave functions. In Henry F. Schaefer, III, editor, *Methods of Electronic Structure Theory*, volume 3 of *Modern Theoretical Chemistry*, page 79. Plenum Press, New York, 1977.
- [13] Weitao Yang and Qin Wu. Direct method for optimized effective potentials in density functional theory. *Physical Review Letters*, 89:143002, 2002.
- [14] Atilla Szabo and Neil S. Ostlund. *Modern Quantum Chemistry*. McGraw-Hill, New York, 1982.
- [15] Michael W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Doseki, Michael S. Gordon K. A. Nguyen, T. L. Windus, and S. T. Elbert. *GAMESS Program Suite*, 1995.
- [16] Schrodinger, Inc. *Jaguar Program Suite*. Portland, Oregon, 5.5 edition, 2003.
- [17] J. P. Perdew, K. Burke, and M. Ernzerhof. Generalized gradient approximation made simple. *Physical Review Letters*, 77(18):3865, 1996.

- [18] S. Bashkin and J. D. Stoner. *Atomic Energy Levels and Groatian Diagrams*. North-Holland, Amsterdam, 1975.
- [19] A. Savin, Cyrus J. Umrigar, and Xavier Gonze. Relationship of Kohn-Sham eigenvalues to excitation energies. *Chemical Physics Letters*, 288:391, 1998.
- [20] G. W. F. Drake and Z. C. Yan. Variational eigenvalues for the S-states of Helium. *Chemical Physics Letters*, 229:486, 1994.
- [21] G. W. F. Drake. In J. Seminario, editor, *Casimir Forces: Theory and Recent Experiments on Atomic Systems*. Elsevier, Amsterdam, 1997.