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SAND2006-0384
Unlimited Release
Printed February 2006

Exchange-Only Optimized Effective Potential Calculation of Excited State Spectra for He and Be Atoms

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(Dated: March 29, 2006)

The optmized effective potential (OEP) method allows orbital-dependent functionals to be used in density functional theory (DFT), which, in particular, allows *exact exchange* formulations of the exchange energy to be used in DFT calculations. Because the exact exchange is inherently self-interaction correcting, the resulting OEP calculations have been found to yield superior band-gaps for condensed-phase systems. Here we apply these methods to the isolated atoms He and Be, and compare to high quality experiments and calculations to demonstrate that the orbital energies accurately reproduce the excited state spectrum for these species. These results suggest that coupling the exchange-only OEP calculations with proper (orbital-dependent or other) correlation functions might allow quantitative accuracy from DFT calculations.

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I. INTRODUCTION

The importance of exact exchange in Kohn-Sham (KS) density functional theory (DFT) was first recognized by Becke (1; 2), who developed *hybrid-exchange* functionals that include a small amount of Hartree-Fock (HF) exchange. These functionals, most notably B3LYP, have shown remarkable accuracy in reproducing, among other things, experimental heats of formation of small molecules. Despite this success, however, HF exchange is an orbital-dependent functional, not a density-dependent functional, and its inclusion in DFT is inconsistent with the theoretical underpinnings (3; 4) of the method.

The optimized effective potential (OEP) method (5) is a technique for obtaining density functionals from orbital-dependent energy functions. Along with the closely-related EXX method of Görling (6–9), these methods have allowed the generation of exchange functionals that derive from the HF exchange energy expression and yet are true density functionals.

There has been considerable hope that these methods will help solve the *band gap* problems that plague HF and DFT. In HF theory, occupied orbitals are properly self-interaction corrected, whereas unoccupied orbitals are not (10), leading to unnaturally high energies for the unoccupied orbitals, and a band gap that is too large. In contrast, in DFT both the occupied and unoccupied orbitals are only self-interaction corrected to the extent that the DFT exchange operator cancels the self-Coulomb interaction. This cancellation is typically imperfect, and DFT typically displays band gaps that are too small, although the fact that both the occupied and unoccupied orbitals display similar errors yields band gaps that are in general closer to the correct values than those from HF theory. The methods based upon OEP or EXX are rigorously self-interaction corrected, and, at the same time, have a consistent treatment of occupied and unoccupied states, giving hope that these approaches will combine the strengths of HF and DFT approaches. Preliminary studies on the computation of band gaps (9; 11; 12), and, in particular, those including a correlated orbital-dependent functional (13; 14), suggest that this hope is well-founded.

This paper reports the excited state spectrum for the atoms He and Be computed with an exchange-only OEP derived functional and compares these values to experimental (15) and theoretical (16) results. This comparison demonstrates that even without inclusion of a correlation function, the exchange-only OEP results in excitation energies that agree very well with experimental and higher-quality theoretical results.

II. METHODS

In the OEP method one writes the KS equations in the form of a kinetic energy operator t and an external potential, which we will denote here as v_{OEP}:

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

The OEP potential v_{OEP} is determined by minimizing an objective energy function, which is taken as the HF energy in the current work. We follow Yang and Wu (17), who define a particularly elegant technique whereby the OEP is expanded in a set of Gaussian functions $g(r)$ about a reference potential $v_0(r)$

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

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

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

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

$$\begin{aligned} \frac{\partial E[\{\phi_i\}]}{\partial v_{OEP}} &= \sum_\ell \frac{\partial E[\{\phi_i\}]}{\partial b_\ell} \\ &= \sum_\ell \sum_{i,a\neq i} \int \frac{\delta E[\{\phi_i\}]}{\delta \phi_i(r)} \phi_a(r) dr \frac{\langle \phi_a | g_\ell | \phi_i \rangle}{\epsilon_i - \epsilon_a} \end{aligned} \tag{4}$$

In the special case of $E[\{\phi_i\}]$ equal to the HF total energy, this equation simplifies to (17)

$$\frac{\partial E^{EXX}[\{\phi_i\}]}{\partial b_\ell} = \sum_{i,a\neq i} \int \left\langle \phi_i \left| F^{HF} \right| \phi_a \right\rangle \frac{\langle \phi_a | g_\ell | \phi_i \rangle}{\epsilon_i - \epsilon_a} \tag{5}$$

where F^{HF} is the Hartree-Fock Fock operator.

We found that very large Gaussian basis sets were required to converge the spectral states we compute. We chose an aug-cc-pVTZ contracted Gaussian basis set (18; 19) for each atom, further augmented with additional diffuse functions. Not surprisingly, the energies of the unoccupied orbitals converged much more slowly than either the total energy or the energy of the occupied orbitals. The final basis set for He had a total of 5 diffuse $s-$, $p-$, and $d-$shells, whereas the basis set for Be had a total of 3 $s-$, $p-$, and $d-$shells. Tables I and II detail our basis sets in full. The final basis set for He contains 65 contracted GTOs, and the final basis set for Be contains 55 contracted GTOs.

The values reported for the BLYP and PBE functionals are computed using the Jaguar Program Suite (20). The other values have been computing using our PyQuante (21) program.

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. The final basis set has 65 contracted Gaussian basis functions.

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

TABLE II Contracted Gaussian basis sets used for Be calculations in this paper. Our basis is a cc-pVTZ basis set, with 3 diffuse $s-$, $p-$, and $d-$shells added to converge the various excited states. The final basis set has 55 contracted Gaussian basis functions.

Core			Valence			Valence			Diffuse		
Type	Exponent	Coefficient	Type	Exponent	Coefficient	Type	Exponent	Coefficient	Type	Exponent	Coefficient
S	6863.000000	0.000236	S	6863.000000	-0.00004	S	0.257700	1.000000	S	0.014697	1.000000
	1030.000000	0.001826		1030.000000	-0.000333	S	0.044090	1.000000	P	0.016647	1.000000
	234.700000	0.009452		234.700000	-0.001736	P	7.436000	0.010736	D	0.060100	1.000000
	66.560000	0.037957		66.560000	-0.007012		1.577000	0.062854	S	0.004899	1.000000
	21.690000	0.119965		21.690000	-0.023126		0.435200	0.248180	P	0.005549	1.000000
	7.734000	0.282162		7.734000	-0.058138	P	0.143800	1.000000	D	0.020033	1.000000
	2.916000	0.427404		2.916000	-0.114556	P	0.049940	1.000000	S	0.001633	1.000000
	1.130000	0.266278		1.130000	-0.135908	D	0.348000	1.000000	P	0.001850	1.000000
	0.110100	-0.007275		0.110100	0.577441	D	0.180300	1.000000	D	0.006678	1.000000

III. RESULTS

In KS DFT, only the highest occupied eigenvalue has a true physical interpretation, corresponding to the negative of the lowest ionization energy. In reference (16), Savin, Umrigar and Gonze derive a nearly exact Kohn-Sham potential from quantum Monte Carlo (QMC) calculations, and

TABLE III Comparison of the Helium experimental excited state spectrum to experimental values (reference (15)) and those resulting from differences in eigenvalues using a high-quality QMC-derived exchange-correlation functional (reference (16)), and those from HF, LDA, BLYP, PBE, B3LYP, and our current OEP/HF approach. The final line reports the mean absolute deviation (MAD) between the QMC-derived exchange-correlation functional and the other techniques.

	Experiment								
State	Triplet	Singlet	QMC	HF	LDA	BLYP	PBE	B3LYP	OEP
1s→2s	0.728	0.758	0.746	0.918	0.571	0.585	0.580	0.662	0.762
1s→2p	0.770	0.780	0.777	0.923	0.576	0.590	0.585	0.667	0.793
1s→3s	0.835	0.842	0.839	0.922	0.574	0.587	0.582	0.665	0.856
1s→3p	0.846	0.848	0.848	0.941	0.592	0.605	0.600	0.683	0.864
1s→3d	0.848	0.848	0.848	0.936	0.589	0.603	0.598	0.680	0.865
1s→4s	0.867	0.870	0.869	0.929	0.580	0.594	0.591	0.673	0.885
MAD				0.107	0.241	0.227	0.232	0.150	0.016

demonstrate that the resulting KS eigenvalues reproduce values from experiment (15) and explicit Hylleraas coordinate calculations of the excited states (22; 23). 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 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 (16) to be the "correct" values.

In the current work we report results using an OEP derived from the HF total energy via equation (5). Although our results do not display the same quantitative agreement with experiment and Hylleraas calculations that those in reference (16) do, our methods come with substantially less computational expense. The accuracy of our results demonstrates that this approach does, in fact, exhibit the correct long-range behavior, and provides hope that, with an appropriate choice of a correlation functional, 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 standard B3LYP functionals. We report the mean absolute deviation (MAD) between the QMC-derived values and those from HF and the DFTs.

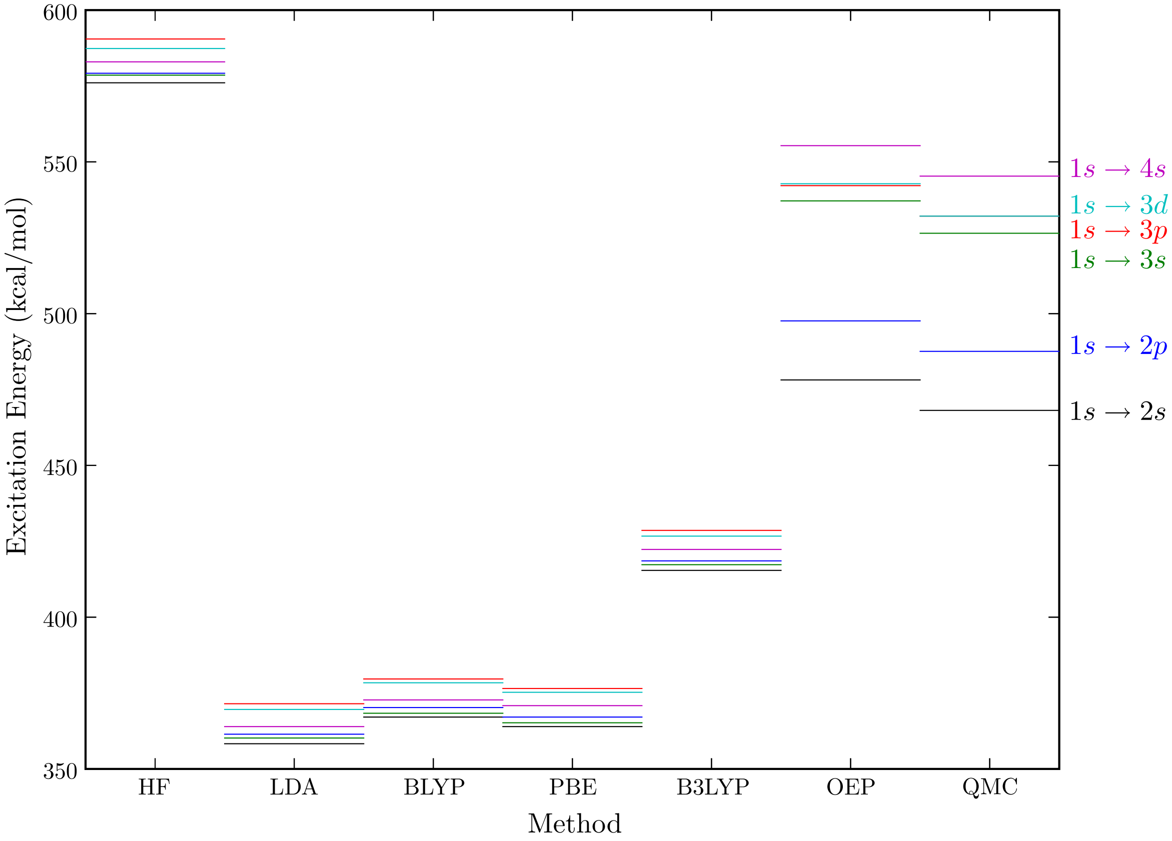

FIG. 1 Comparison of excitation energies for He atom computed from the KS-DFT eigenvalues using HF, LDA, BLYP, PBE, B3LYP, OEP, and QMC exchange-correlation functionals. The colors denote the excitation level, as labeled on the right.

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 function has a MAD of 0.15 h. Our exchange-only OEP values differ by only 0.016 h, nearly a factor of 10 better than the best of the standard DFTs. Moreover, the OEP values differ from the QMC values by almost a constant value of 0.016 h across the entire spectrum, whereas the LDA, GGA, and HF values fluctuate much more about their average deviation. These spectra are shown graphically in Figure 1. This figure illustrates that not only are the OEP values better on the average, but each individual excitation level differs from the corresponding exact value by a near-constant shift.

Table IV reports a similar comparison for the Beryllium excitation energies. On the average the HF excitation energies differ by 0.075 h, the LDA, BLYP, and PBE values differ by 0.050-0.070, and the B3LYP values differ by 0.038 h. In contrast, the exchange-only OEP values differ by only 0.004 h, nearly a factor of ten smaller average difference than the best of the standard DFTs. Moreover, as was seen in He, the OEP excitation energies differ from the QMC values by a constant shift, whereas the LDA, GGA, and HF values fluctuate much more about their averages. These spectra

TABLE IV Comparison of the Beryllium experimental excited state spectrum to experimental values (reference (15)) and those resulting from differences in eigenvalues using a high-quality QMC-derived exchange-correlation functional (reference (16)), and those from HF, LDA, BLYP, PBE, B3LYP, and our current OEP/HF approach. The final line reports the mean absolute deviation (MAD) between the QMC-derived exchange-correlation functional and the other techniques.

	Experiment								
State	Triplet	Singlet	QMC	HF	LDA	BLYP	PBE	B3LYP	OEP
2s→2p	0.100	0.194	0.133	0.313	0.129	0.130	0.132	0.180	0.130
2s→3s	0.237	0.249	0.244	0.312	0.205	0.198	0.204	0.230	0.240
2s→3p	0.268	0.274	0.269	0.325	0.210	0.204	0.210	0.236	0.267
2s→3d	0.283	0.294	0.283	0.331	0.220	0.214	0.220	0.246	0.278
2s→4s	0.294	0.297	0.296	0.321	0.211	0.206	0.212	0.238	0.292
MAD				0.075	0.050	0.055	0.050	0.038	0.004

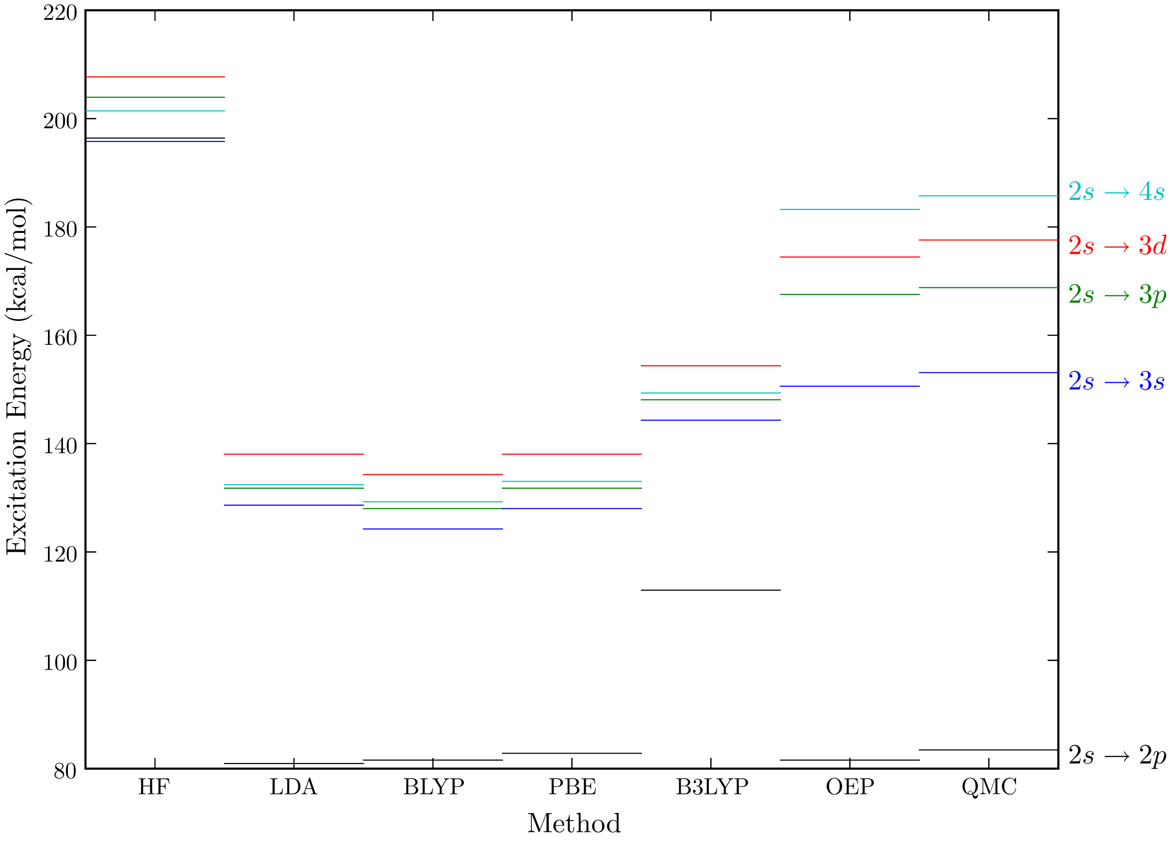

FIG. 2 Comparison of excitation energies for Be atom computed from the KS-DFT eigenvalues using HF, LDA, BLYP, PBE, B3LYP, OEP, and QMC exchange-correlation functionals. The colors denote the excitation level, as labeled on the right.

are shown graphically in Figure 2, which again illustrates that not only does the OEP perform better on the average, but that each individual excitation value once again differs from the exact levels by a small, nearly constant shift.

We believe it significant that for the He and Be spectrum the OEP excitation levels differ from the exact levels by a nearly constant amount. Clearly, the HF description on which our OEP is based omits the correlation energy, and the high accuracy of the excitation levels and the regularity of the error gives hope that simple models for the electron correlation might further reduce the overall error.

IV. CONCLUSION

This paper has demonstrated that the exchange-only OEP functional does a remarkably good job of reproducing excitation energies for the He and Be atoms. We believe this accuracy is a result of the correct long-range behavior of the orbitals, arising from the proper self-interaction correction of the exact exchange. The exchange-only OEP excitation energies differ from those produced by QMC-derived exchange-correlation functionals by only 0.016 h for He, and 0.004 h for Be. The fact that Hartree-Fock, a very simple orbital-dependent functional, shows such accuracy suggests that a more sophisticated energy functional containing some amount of electron correlation might realize quantitatively accurate DFT calculations at a modest computational expense. Indeed, Bartlett and coworkers (13; 14) use of many-body perturbation theory for the correlation energy in OEP calculations has shown impressive results for ground-state energies and energy gaps.

V. ACKNOWLEDGMENTS

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 Daniel Rohr for helpful discussions on OEP, and John Aidun, Peter Schultz and Cyrus Umrigar for helpful comments on our 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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