Additive atomic approximation for relativistic effects: a two-component Hamiltonian for molecular electronic structure calculations

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An approximate relativistic two-component Hamiltonian for use in molecular electronic structure calculations is derived in the form of a sum of fixed atom-centered kinetic and spin-orbit operators added to the non-relativistic Hamiltonian. Starting from the well-known zeroth-order regular approximation, further steps are taken to get rid of its nonlinearity in the potential, ending up with a simple formulation with easily computable integrals that can seamlessly work with any traditional electronic structure method. Molecular tests show a good accuracy of this approximation.

Even though the Dirac equation is the best theory of the electron, its simple nonrelativistic approximation — the Schrödinger equation — is most widely used in molecular electronic structure calculations. When it comes to heavier atoms, the effective core potentials most often come into play, as they can model, albeit in a rather queer way, the relativistic effects felt by the valence electrons; besides their quite arbitrary parametrization, they may suffer from numerical instability and need a special care in the evaluation of their integrals over the traditional Gaussian functions.

Another two-component formalism, until now limited only to density-functional methods, is the zeroth-order regular approximation\textsuperscript{6, 7} that works with a local effective one-electron potential in such a nonlinear way that it cannot deal with the more general many-electron wavefunction theories. We have found, however, a further approximation that removes this nonlinearity and leads to a very simple one-electron Hamiltonian for molecular electronic structure theories, the straightforward analytical evaluation of its matrix elements over the Gaussian basis sets allows it to be easily implemented into quantum chemistry codes for both correlated-wavefunction and density-functional calculations. We are glad to report it here, along with the construction of atomic basis sets of our correlation-consistent type. We test its performance on some characteristic molecular examples using the coupled-cluster\textsuperscript{8–12} theory with single and double\textsuperscript{10} (CCSD) substitutions.

For an electron in a potential \( v(\mathbf{r}) \) the Dirac equation can be written as

\[
\begin{cases}
(v(\mathbf{r}) - \epsilon) \psi_\text{S}(\mathbf{r}) + \frac{\sigma \cdot \mathbf{p}}{2c^2} \psi_\text{L}(\mathbf{r}) = 0 \\
v(\mathbf{r}) - 2c^2 - \epsilon) \psi_\text{L}(\mathbf{r}) + \frac{\sigma \cdot \mathbf{p}}{2c^2} \psi_\text{S}(\mathbf{r}) = 0
\end{cases}
\]  

(1)

with the Pauli matrices

\[
\sigma = \begin{pmatrix}
0 & 1 \\
1 & 0
\end{pmatrix}, \begin{pmatrix}
0 & -i \\
i & 0
\end{pmatrix}, \begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}.
\]

(2)

The relation between the small \( \psi_\text{S}(\mathbf{r}) \) and large \( \psi_\text{L}(\mathbf{r}) \) component wavefunctions from the second line of Eq. (1)

\[
\psi_\text{S}(\mathbf{r}) = \frac{c}{2c^2 - v(\mathbf{r}) + \epsilon} \sigma \cdot \mathbf{p} \psi_\text{L}(\mathbf{r})
\]

(3)

can be simplified and approximated by dropping out the energy \( \epsilon \) in the denominator of Eq. (3), as for the valence electrons in molecules \( \epsilon \ll 2c^2 \) and a typically attractive effective potential \( v(\mathbf{r}) < 0 \). Putting the approximate \( \psi_\text{S}(\mathbf{r}) \) into the first line of Eq. (1) leads to the two-component relativistic equation

\[
\left( v(\mathbf{r}) + \sigma \cdot \mathbf{p} \frac{c^2}{2c^2 - v(\mathbf{r})} \sigma \cdot \mathbf{p} \right) \psi(\mathbf{r}) = \epsilon \psi(\mathbf{r})
\]

(4)

that works only with the large component \( \psi(\mathbf{r}) = \psi_\text{L}(\mathbf{r}) \), the well-known zeroth-order regular approximation\textsuperscript{16}.

The appearance of \( v(\mathbf{r}) \) in Eq. (4) in a non-linear way besides the usual multiplicative potential limits the applications of this formalism to the local-potential models of density-functional theory, where the effective potential is solved for self-consistently together with the one-electron wavefunctions if depends on. Now we will make further approximations to get rid of this non-linearity by making the relativistic correction term independent of the molecular electronic structure.

The Hamiltonian of Eq. (4) can be written

\[
\hat{H} = v(\mathbf{r}) - \frac{\sigma \cdot \mathbf{p}}{2c^2} u(\mathbf{r}) \sigma \cdot \mathbf{p} = \hat{H}_0 + \hat{H}_u
\]

(5)

as a sum of the non-relativistic \( \hat{H}_0 \) and the relativistic correction \( \hat{H}_u \) with the scalar function

\[
u(\mathbf{r}) = \frac{v(\mathbf{r})}{2c^2 - v(\mathbf{r})}
\]

(6)

that for \( v(\mathbf{r}) \leq 0 \) has the range \(-1 \leq u(\mathbf{r}) \leq 0\) and plays a role mostly in the atomic core regions, as \(- v(\mathbf{r}) \ll 2c^2\) elsewhere. We approximate \( v(\mathbf{r}) \) in Eq. (6) by a sum of fixed non- (or weakly) overlapping spherically-symmetric atom-centered potentials

\[
\tilde{v}(\mathbf{r}) = \sum_k v_k |\mathbf{r} - \mathbf{r}_k|
\]

(7)

\[
\sum_k v_k |\mathbf{r} - \mathbf{r}_k|
\]
then \( u(\mathbf{r}) \) can be given in the same way as

\[
  u(\mathbf{r}) = \sum_k u_k(|\mathbf{r} - \mathbf{r}_k|),
\]

(8)

our localized atomic radial functions

\[
  u_k(r) = b(r) \frac{v_k(r)}{2\epsilon^2 - v_k(r)}
\]

(9)

further have a cut-off factor

\[
  b(r) = \begin{cases} 
    1, & \text{if } r < r_1 \\
    \frac{1}{3} s((2r - r_0 - r_1)/(r_0 - r_1)), & r_1 \leq r \leq r_0 \\
    0, & \text{if } r > r_0
  \end{cases}
\]

(10)

that brings them smoothly to zero for \( r > r_0 \).

We take \( v_k(r) \) in Eq. (9) as the purely electrostatic potential of the nuclear charge and electron density from the spherically-symmetric average-level\(^{20}\) Hartree-Fock calculations on the neutral atoms within the scalar-relativistic approximation\(^{42}\) of the Dirac-Coulomb Hamiltonian — as such, it has an exponentially-decaying tail that can be easily bent down to zero. Had we added a local exchange potential, there would have been either a very long tail for an asymptotically correct local exchange potential, there would have been either a very long tail for an asymptotically correct \( v_k(r) \to -1/r \) as \( r \to \infty \), or a mild deepening of \( v_k(r) \) mostly where we are going to cut it down. Moreover, the lack of the exchange term may somewhat compensate for the energy dropped in the denominator of Eq. (10).

In Eq. (10) we use our favorite switching function

\[
  s(x) = \tanh \left( \sqrt{3} \frac{x}{1 - x^2} \right)
\]

where the factor of \( \sqrt{3} \) makes the third derivative \( s'''(0) = 0 \), and we find the cut-off limits \( r_1 = \frac{1}{3} \) and \( r_0 = \frac{1}{2} \) to yield the rather smooth \( u_k(r) \) from Eq. (10), for all atoms, without inflection points between \( r_1 \) and \( r_0 \). We have tried to find a better cut-off factor, for example, a more general function could be used with parameters adjusted to minimize some criterion, but it did not yield a better output of the whole work.

Our last step is to make the integrals of the Hamiltonian of Eqs. (5) and (8) over the traditional Gaussian basis sets easy to compute analytically, so we further approximate \( u_k(r) \) from Eq. (9) by sums of Gaussians

\[
  u_k(r) \approx \hat{u}_k(r) = \sum_{i=1}^{n} c_{ik} \exp (-a_{ik} r^2)
\]

(12)

with parameters \( \{c_{ik}\} \) and \( \{a_{ik}\} \) from the least-squares minimization

\[
  \int_0^{\infty} |\hat{u}_k(r) - u_k(r)|^2 \, dr = \text{min}.
\]

(13)

We find \( n = 15 \) in Eq. (12) to be the best for all atoms, it is the greatest \( n \) for which all \( c_{ik} \) are still negative, the smallest \( a_{1k} \) falls in the range \( 2.4 < a_{1k} < 3.6 \) with \( |c_{1k}| < 0.002 \), and the fit error \( \mu = \max_r |\hat{u}_k(r) - u_k(r)| < 0.0011 \). Another good \( n = 17 \) has \( \mu < 0.00007 \) thanks to a better fit at a very short \( r \) with one positive \( c_{ik} \), but it makes only a slight change in the computed atomic wavefunctions. For comparison, we have also made very accurate fits with \( 38 \leq n \leq 50 \) for the uncut \( u_k(r) \) with \( b(r) \equiv 1 \) in Eq. (7), and the atomic calculations show that by far the greatest change comes when the two-component Eq. (1) is used instead of the four-component Eq. (1), the cut-off function of Eqs. (10) and (11) has then only a slight effect, and even less so does the 15-term fit of Eq. (12).

The relativistic Hamiltonian term \( \hat{H}_\alpha \) of Eq. (5) can be split into a “scalar” part

\[
  \hat{H}_s = -\frac{1}{2} \nabla \cdot u(\mathbf{r}) \nabla
\]

(14)

that can be thought of as a rescaling of the kinetic energy, and a “vector” part

\[
  \hat{H}_v = -\frac{i}{2} \sigma \cdot \left( (\nabla u(\mathbf{r})) \times \nabla \right)
\]

(15)

that leads to the spin-orbit coupling. With \( \hat{H}_s \) only, we get a scalar-relativistic approximation that can seamlessly work with any traditional non-relativistic electronic structure method to allow the studies of molecules with heavier atoms, we would call it an additive atomic approximation (AAA), and we implement it first into our computer code. The spin-orbit term \( \hat{H}_v \) can be treated as a perturbation, and we believe our function \( u(\mathbf{r}) \) to be a sound choice for this.

Throughout our work, we use the newest estimate\(^{21,22}\) of the speed of light \( c = 137.035999173 \) and the finite nucleus mode\(^{23}\) with Gaussian charge distribution with the exponent (in au)

\[
  \alpha = \frac{\pi}{2} \left( \frac{529177249}{5700 + 8360 \cdot \sqrt{M}} \right)^2
\]

(16)

where \( M \) is the (integer) mass number of the most abundant isotope.

We run our atomic electronic structure code\(^{14}\) working in 256-bit precision, first to get the nearly-exact four-component scalar-relativistic\(^{20}\) spherically-symmetric atomic Hartree-Fock solutions over the huge even-tempered Gaussian basis sets, for all 102 atoms from Hydrogen through Nobelium. Then we compute the values of function \( u_k(r) \) from Eq. (9) on a very dense grid of points in the spirit of double-exponential integration\(^{24}\), and get the 15-term Gaussian fits of Eqs. (12) minimizing the integral of Eq. (13) computed numerically on the grid; we check the goodness of the fit by plotting, for all atoms, the difference \( \hat{u}_k(r) - u_k(r) \) as a function of \( \ln(r) \) and also the values of \( \ln(u_k(r)) \) against the atomic number, and see that it is good. These values of \( \{c_{ik}\} \) and \( \{a_{ik}\} \) are tabulated to 20 decimal places in the supplementary materials\(^{25}\) and everyone is welcome to use them.

For our AAA Hamiltonian, we get our correlation-consistent atomic basis sets, for all 102 atoms, in the
TABLE I. Molecular properties computed by CCSD/L2.4.  

| mol. | $\hat{R}^a$ | $E$ | mol. | $\hat{R}^a$ | $E$ |
|------|-------------|-----|------|-------------|-----|
| LiH  | 4           | 3.0216 0.09070 | Li$_2$ 4 | 5.0684 0.03785 |
|      | 2           | 3.0217 0.09070 | 2      | 5.0685 0.03785 |
|      | n           | 3.0218 0.09070 | n      | 5.0688 0.03785 |
| NaF  | 4           | 3.5742 0.07800 | Na$_2$ 4 | 5.8783 0.02564 |
|      | 2           | 3.5745 0.07800 | 2      | 5.8789 0.02564 |
|      | n           | 3.5757 0.07803 | n      | 5.8864 0.02563 |
| KH   | 4           | 4.2632 0.06406 | K$_2$ 4 | 7.5392 0.01682 |
|      | 2           | 4.2635 0.06407 | 2      | 7.5403 0.01682 |
|      | n           | 4.2700 0.06426 | n      | 7.5664 0.01685 |
| RbH  | 4           | 4.5019 0.06184 | Rb$_2$ 4 | 8.1152 0.01418 |
|      | 2           | 4.5023 0.06185 | 2      | 8.1169 0.01418 |
|      | n           | 4.5023 0.06185 | n      | 8.1175 0.01418 |
| CsH  | 4           | 4.7620 0.06335 | Cs$_2$ 4 | 9.0258 0.01201 |
|      | 2           | 4.7611 0.06335 | 2      | 9.0263 0.01200 |
| CuH  | 4           | 2.7694 0.09856 | Cu$_2$ 4 | 4.2797 0.03978 |
|      | 2           | 2.7705 0.09846 | 2      | 4.2813 0.03881 |
|      | n           | 2.8195 0.09842 | n      | 4.3487 0.06023 |
| AgH  | 4           | 3.0614 0.08412 | Ag$_2$ 4 | 4.8571 0.05214 |
|      | 2           | 3.0636 0.08427 | 2      | 4.8597 0.05200 |
|      | n           | 3.0658 0.08432 | n      | 4.8614 0.05200 |
| AuH  | 4           | 2.8758 0.11323 | Au$_2$ 4 | 4.7387 0.07089 |
|      | 2           | 2.8791 0.11220 | 2      | 4.7461 0.06990 |
| HF   | 4           | 1.7271 0.21599 | F$_2$ 4 | 2.6481 0.03978 |
|      | 2           | 1.7270 0.21605 | 2      | 2.6481 0.03979 |
|      | n           | 1.7271 0.21631 | n      | 2.6476 0.03984 |
| HCl  | 4           | 2.4098 0.16321 | Cl$_2$ 4 | 3.7910 0.07483 |
|      | 2           | 2.4098 0.16324 | 2      | 3.7910 0.07486 |
|      | n           | 2.4100 0.16360 | n      | 3.7979 0.07516 |
| HBr  | 4           | 2.6771 0.14198 | Br$_2$ 4 | 4.3469 0.06580 |
|      | 2           | 2.6773 0.14199 | 2      | 4.3473 0.06583 |
|      | n           | 2.6811 0.14294 | n      | 4.3518 0.06606 |
| HI   | 4           | 3.0513 0.12100 | I$_2$ 4 | 5.0993 0.05860 |
|      | 2           | 3.0524 0.12106 | 2      | 5.0991 0.05868 |
|      | n           | 3.0527 0.12109 | n      | 5.0992 0.05865 |
| Sb$_2$ | 4           | 4.7403 0.07654 | UO$_3$ 4 | 3.3565 |
|      | 2           | 4.7426 0.07650 | 2      | 3.3462 |
|      | n           | 4.7426 0.07650 | n      | 3.3462 |
| Bi$_2$ | 4           | 5.0248 0.05964 | 4      | 3.4667 |
|      | 2           | 5.0394 0.05932 | 2      | 3.4624 |

$\text{Hamiltonian: 4 four-, 2 two-component, n non-relativistic.}$

Bond lengths $r$ and bond energies $\Delta E$ are in au.

well matched to the density functional methods of generalized-gradient type$^{26,27}$ and beyond$^{28,29}$, we have already implemented it into our density-functional code$^{31}$ through analytic second derivatives.

The molecular properties
computed therewith can be compared one-to-one with those based on the four-component scalar-relativistic Hamiltonian, and even more so for the longer underlying primitive sets.

Table 1 shows our tests on a small but representative set of molecules using the CCSD/L2 method and the L2.4 basis set. The bond lengths and bond energies (with excitation zero-point vibrations) begin to differ between the nonrelativistic and the four-component scalar-relativistic theories on going to heavier atoms, while our new two-component approximation brings them close to the latter, and although it becomes slightly worse for the heaviest atoms, it is still rather good.

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ture calculations using different nuclear charge distributions,” Atom. Data Nucl. Data, 67, 207 (1997).
24H. Takahasi and M. Mori, “Double exponential formulas for numerical integration,” Publ. RIMS Kyoto Univ., 9, 721 (1974).
25Supplementary material.
26A. D. Becke, “Density-functional exchange-energy approximation with correct asymptotic behavior,” Phys. Rev. A, 38, 3098 (1988).
27J. P. Perdew, K. Burke, and M. Ernzerhof, “Generalized gradient approximation made simple,” Phys. Rev. Lett., 77, 3865 (1996).
28J. Tao, J. P. Perdew, V. N. Staroverov, and G. E. Scuseria, “Climbing the density functional ladder: Nonempirical meta-
29M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, “Van der waals density functional for general geometries,” Phys. Rev. Lett., 92, 246401 (2004).
30O. A. Vydrov and T. van Voorhis, “Nonlocal van der Waals density functional: The simpler the better,” J. Chem. Phys., 133, 244103 (2010).
31D. N. Laikov, “Fast evaluation of density functional exchange-correlation terms using the expansion of the electron density in auxiliary basis sets,” Chem. Phys. Lett., 281, 151 (1997).