# Analysis of the contributions to the kinetic and potential energies of an H atom in the presence of a point charge: the molecular virial theorem revisited

Arailym Kairalapova and Kenneth D. Jordan*

*University of Pittsburgh, Pittsburgh, PA 15260*

E-mail: jordan@pitt.edu

## Abstract

The molecular virial theorem states that for a diatomic molecule or for an atom in the presence of a point charge, the changes in the average kinetic energy and average potential energy are equal to $\langle T \rangle = -U - R\frac{dU}{dR}$ and $\langle V \rangle = 2U + R\frac{dU}{dR}$, respectively, where $U$ is the interaction energy and $R$ is the internuclear separation or the atom-point charge separation. In this paper we directly evaluate the $\langle T \rangle$ and $\langle V \rangle$ expectation values of an H atom in the presence of a distant point charge, obtaining exact analytical expressions by use of Dalgarno-Lewis perturbation theory.

## Introduction

For atoms as well as molecular systems at their equilibrium structures the virial theorem states that

$$\langle T \rangle = -\frac{1}{2} \langle V \rangle, \tag{1}$$

where $T$ and $V$ denote the kinetic and potential energy operators, respectively. The virial theorem is necessarily obeyed for the exact wave function, whereas approximate wave functions can give average kinetic and potential energies that significantly deviate from obeying the virial theorem. The virial theorem was generalized to diatomic molecules at arbitrary internuclear separation by Slater[1] and subsequently by Hurley[2] to polyatomic molecules at arbitrary geometries to give the so-called molecular virial theorem. These generalizations assumed the validity of the Born Oppenheimer approximation.[3] For diatomic molecules at an arbitrary bond length Slater obtained

$$\langle T \rangle = -E - R\frac{dE}{dR}, \tag{2a}$$

$$\langle V \rangle = 2E + R\frac{dE}{dR}, \tag{2b}$$

where $E$ is the total energy and $R$ is the internuclear separation. The changes in the average kinetic and potential energies due to the interaction is

$$\Delta \langle T \rangle = \langle T \rangle - \langle T \rangle_\infty = -U - R\frac{dU}{dR}, \tag{3a}$$

$$\Delta \langle V \rangle = \langle V \rangle - \langle V \rangle_\infty = 2U + R\frac{dU}{dR}, \tag{3b}$$

where $\langle T \rangle_\infty$ and $\langle V \rangle_\infty$ refer to the averages at infinite internuclear separation and $U$ is the interaction energy. Thus for a neutral diatomic molecule at $R$ values for which $C_6$ dispersion dominates

$$\Delta \langle T \rangle = 5U, \tag{4a}$$

$$\Delta \langle V \rangle = -4U. \tag{4b}$$

Interestingly, while a second-order perturbation theory treatment describes the long-range dispersion interaction purely in terms of the dipole-dipole coupling, the virial theorem indicates that the potential energy contribution is repulsive and that the net attraction is actually a consequence of the kinetic energy.

In general, one determines the average kinetic energy and potential energy contributions by fitting the interaction energies from electronic structure calculations as a function of $R$ and using Eq. 3 rather than by directly calculating expectation values of the $T$ and $V$ operators.

In order to obtain a better understanding of the origin of the attractive kinetic energy and repulsive potential energy contributions predicted by the virial theorem, it is useful to consider the simpler problem of an H atom in the field of a point charge, at a distance $R$ from the atom, as well as in a uniform electric field, since exact, complete basis set results can be obtained for these cases. In the limit that only dipole polarization is important, the molecular virial theorem (Eq. 3) gives

$$\Delta \langle T \rangle = 3U, \tag{5a}$$

$$\Delta \langle V \rangle = -2U. \tag{5b}$$

For a positive point charge, $|e|$, this corresponds to the $H_2^+$ molecular ion with the neglect of charge delocalization, the long-range behavior of which has been the subject of numerous studies.[4–7] However, here our focus is on analyzing the field-induced shifts in the average kinetic and potential energies in terms of contributions to the wave function in the complete basis set limit and which are obtained by use of Dalgarno-Lewis perturbation theory.[4] Of course, the H atom in the presence of a uniform efield, has no bound states,[8] but for the calculations presented here autoionization is not an issue: for the complete basis set analytical results it is suppressed by the use of low-order perturbation theory, and for the finite basis set variational calculations it is suppressed by the limited spatial extent of the basis functions.

At large separation, $R$, of the point charge from the atom, the sign of the point charge is immaterial and

$$U = -\frac{\alpha}{2R^4}, \tag{6}$$

where $\alpha$ is the dipole polarizability. In the complete basis set limit $\alpha = -4.5$ a.u. and $U = -2.25R^{-4}$ a.u.[4] For the case of an atom in a uniform electric field, the analog of the molecular virial theorem is

$$\Delta \langle T \rangle = -U + 2\varepsilon \frac{dU}{d\varepsilon}, \tag{7a}$$

$$\Delta \langle V \rangle = 2U - 2\varepsilon \frac{dU}{d\varepsilon}, \tag{7b}$$

where $U = -0.5\alpha\varepsilon^2$

# Theory

Although our primary interest is in delineating the various contributions to $\Delta \langle T \rangle$ and $\Delta \langle V \rangle$ as evaluated directly from the wave function, we find it instructive to first consider results obtained from finite basis set variational calculations. For these calculations we employ for the H atom a basis set comprised of the $s$ and $p$ portions of the aug-cc-pV6Z Gaussian-type orbital basis set.[9,10] This basis set (hereafter referred to as **A**) gives an energy of the ground state of the isolated H atom only $7 \times 10^{-7}$ a.u. above the exact value and a value of the dipole polarizability of 4.4928 a.u., in close agreement with the exact result of 4.5 a.u. We place the perturbing point charge, here taken to be $q = -|e|$, 10 Bohr from the H atom which results in an electric field of 0.01 a.u. The efield calculations were carried out on the H atom using this field strength. The finite-basis set calculations were carried out using the Gaussian 16 program.[11]

Table 1 reports the total energy, the $\langle V \rangle$ and $\langle T \rangle$ values, and the virial ratio of the isolated atom as well as for the atom in the presence of the point charge or the uniform electric field as obtained from the finite basis set calculations. For comparison the Table also reports exact results obtained in the complete basis set limit, calculated allowing only dipole polarization. (The procedure used to obtain the exact results is described below.) To facilitate analysis of the results, the Table also reports the changes in $\langle T \rangle$ and $\langle V \rangle$ caused by the perturbations.

From Table 1, it is seen that with basis set **A** the variational calculations on the H atom in the presence of the point charge or the external uniform efield give $\langle V \rangle / \langle T \rangle$ ratios and $\Delta \langle T \rangle$ and $\Delta \langle V \rangle$ values very close to the exact results. The small discrepancies of the finite basis set variational results from the exact results (described below) are due to the incompleteness of the basis set (in the $s$ and $p$ space) as well as to the recovery in the former of contributions other than dipole polarization. Specifically, at the value of $R$ and field strength employed in the calculations, there is a small contribution from the $\gamma$ hyperpolarizability, and in the point charge calculations there is also a more significant contribution from the $B$ dipole-dipole-quadrupole hyperpolarizality. These higher-order contributions would cease to be important were $R$ increased to say 20 Bohr and the external field to 0.0025 a.u.

A clue as to the terms in the wave function responsible for the changes in $\langle V \rangle$ and $\langle T \rangle$ due to the point charge or external efield is provided by the following "experiment". We uncontracted the $s$ functions in basis set **A**, and used the resulting set of primitive functions in a variational calculation of the energy of the isolated H atom. The $s$ primitives were then contracted to a single function with the contraction coefficients being taken to correspond to those of the $1s$ orbital from the variational calculation. We now make a new basis set, designated **B**, by combining the single contracted $s$ function with the six $p$ functions of basis set **A**. Calculations with basis set **B** give the same energy and dipole polarizability of the isolated H atom as basis set **A**. However, they give much smaller in magnitude $\Delta \langle T \rangle$ and $\Delta \langle V \rangle$ values and an appreciably different virial ratio than obtained using basis set **A**. Thus a basis set with multiple $s$ functions rather than the single contracted $s$ function is important in establishing the virial theorem result. Indeed, it has been noted in prior studies that the lowering of the kinetic energy of $H_2^+$ at large $R$ is associated with a delocalization of the electron density.[7]

We now progress to a detailed analysis of the various contributions to the kinetic energy and potential energy resulting from the perturbation (point charge or uniform efield). The ground state wave function of the H atom in the presence of the point charge or efield may be expressed as in terms of the orbitals of the unperturbed H atom as

$$\psi = |1s\rangle + \sum_{n=2} c_n^{(p)} |np\rangle + \sum_{n\neq 1} c_n^{(s)} |ns\rangle, \tag{8}$$

where only $s$ and $p$ basis functions are included as we are focusing on dipole polarization. The coefficients in Eq. 8 are given by

$$c_n^{(p)} = \frac{\langle np|V'|1s\rangle}{\epsilon_{1s} - \epsilon_{np}} \tag{9}$$

and

$$c_n^{(s)} = \sum_{m=2} \frac{\langle ns|V'|mp\rangle\langle mp|V'|1s\rangle}{(\epsilon_{1s} - \epsilon_{ns})(\epsilon_{1s} - \epsilon_{mp})}. \tag{10}$$

In Eqs. 9 and 10 and ensuing equations, $V'$ denotes the external perturbation, and the orbitals and orbital energies are the exact results for the non-relativistic Schrödinger equation (the Hamiltonian of which is denoted by $H^0$) for the H atom. In addition, the sums also include the continuum contributions.

If we retain energy contributions through second-order in the perturbation, the energy lowering relative to that of an isolated H atom (i.e., $\langle 1s|H^0|1s\rangle$) is

$$\sum_{n=2} \Big[ c_n^{(p)^2} (\langle np|H^0|np\rangle - \langle 1s|H^0|1s\rangle) + 2c_n^{(p)} \langle np|V'|1s\rangle \Big] \tag{11}$$

which, upon the substitution,

$$\langle np|H^0|np\rangle - \langle 1s|H^0|1s\rangle = \epsilon_{np} - \epsilon_{1s}, \tag{12}$$

reduces to

$$\sum_{n=2} \frac{\langle 1s|V'|np\rangle\langle np|V'|1s\rangle}{\epsilon_{1s} - \epsilon_{np}} \tag{13}$$

which is the standard second-order perturba-

**Table 1: Energies (a.u.) virial ratios, $\langle V\rangle$, and $\langle T\rangle$ values (in a.u.) of an H atom, both isolated, and in the presence of a $-|e|$ point charge at $R = 10$ Bohr or a uniform electric field of strength 0.01 a.u.**

| System | Basis set | $E_{tot}$ | $-\frac{\langle V\rangle}{\langle T\rangle}$ | $\langle V\rangle$ | $\langle T\rangle$ | $\Delta\langle V\rangle$ | $\Delta\langle T\rangle$ |
|---|---|---|---|---|---|---|---|
| isolated[a] | CBS[b] | -0.5000000 | 2.000000 | -1.0000000 | 0.5000000 | | |
| efield, pt. chg. | CBS[b] | -0.5002250 | 2.001802 | -0.9995500 | 0.4993250 | 0.0004500 | -0.0006750 |
| isolated[a] | **A**, **B** | -0.4999993 | 2.000004 | -0.9999966 | 0.4999973 | | |
| efield | **A** | -0.5002242 | 2.001811 | -0.9995441 | 0.4993200 | 0.0004559 | -0.0006800 |
| efield | **B** | -0.5002238 | 2.000653 | -1.0001211 | 0.4998973 | -0.0001211 | -0.0001027 |
| pt. chg. | **A** | -0.5002218 | 2.001779 | -0.9995554 | 0.4993337 | 0.0004446 | -0.0006663 |
| pt. chg. | **B** | -0.5002214 | 2.000640 | -1.0001229 | 0.4999015 | -0.0001229 | -0.0000985 |

[a] Isolated H atom.

[b] Exact results in the complete $s$ and $p$ basis set (CBS) limit, allowing only for dipole polarization.

tion result. Dalgarno and Lewis[4] showed that for a perturbation of the form $D\,r\cos\theta$, where $D = q/R^2$ and $\varepsilon$ for the point charge and uniform fields, respectively, one can find a function $f = D(r^2/2 + r)\cos\theta$ such that

$$\begin{aligned}\langle np|V'|1s\rangle &= \langle np|[H^0, f]|1s\rangle \\ &= (\epsilon_{np} - \epsilon_{1s})\langle np|f|1s\rangle, \end{aligned} \tag{14}$$

allowing Eq. 13 to be rewritten as

$$-\sum_{n=2}\langle 1s|V'|np\rangle\langle np|f|1s\rangle = -\langle 1s|V'f|1s\rangle. \tag{15}$$

Elimination of the the $\sum|np\rangle\langle np|$ summation in the left-hand side of Eq. 15 was accomplished by use of the identity operator, which for the H atom is

$$1 = |1s\rangle\langle 1s| + \sum_{n\neq 1}|ns\rangle\langle ns| + \sum_{n=2}|np\rangle\langle np| + \ldots\ . \tag{16}$$

Specifically $\sum|np\rangle\langle np|$ was replaced by 1, as the other terms in the expansion do not result in non-zero integrals. The resulting integral on the right-hand side of Eq. 15 may be readily evaluated, giving $-2.25R^{-4}$ for the point charge perturbation and $-2.25\varepsilon^2$ a.u. for the uniform efield perturbation.[4]

We now consider the contributions of the various terms in the wave function to the averages of the kinetic energy operator and the $-1/r$ portion of the potential energy operator, retaining terms that are second-order in the interaction. The relevant averages are given by

$$\begin{aligned}\Delta\left\langle \hat{A}\right\rangle = &-\sum_{n=2}(c_n^{(p)})^2\langle 1s|\hat{A}|1s\rangle \\ &+\sum_{\substack{n=2,\\ m=2}} c_n^{(p)}c_m^{(p)}\langle np|\hat{A}|mp\rangle \\ &+2\sum_{n\neq 1} c_n^{(s)}\langle ns|\hat{A}|1s\rangle, \end{aligned} \tag{17}$$

where $\hat{A}$ denotes either the kinetic energy operator or $-1/r$. The first term on the right-hand side of Eq. 17 is a result of normalization, which may be evaluated as follows

$$\begin{aligned}&-\sum_{n=2}\langle 1s|f|np\rangle\langle np|f|1s\rangle\langle 1s|\hat{A}|1s\rangle \\ &= -\langle 1s|f^2|1s\rangle\langle 1s|\hat{A}|1s\rangle. \end{aligned} \tag{18}$$

In accomplishing this simplification we made use of the fact that the $(c_n^{(p)})^2$ factor in Eq. 17 can be rewritten as $\langle 1s|f|np\rangle\langle np|f|1s\rangle$ by two applications of the Dalgarno-Lewis procedure again with $f = D(r^2/2 + r)\cos\theta$, and the replacement of $\sum|np\rangle\langle np|$ with 1 as discussed above. The two integrals in the right-most term of Eq. 18, $\langle 1s|f^2|1s\rangle$ and $\langle 1s|\hat{A}|1s\rangle$, are readily evaluated with the results being presented in Table 2 below.

The second term on the right-hand side of

**Table 2: Contributions to $\Delta\langle T\rangle$ and $\Delta\langle V\rangle$ for a H atom perturbed by a point charge or a uniform efield evaluated in the complete basis set limit.[a]**

| Contribution | $\Delta\langle T\rangle$ | $\Delta\langle V\rangle$ |
|---|---|---|
| $-\sum(c_n^{(p)})^2\langle 1s\lvert\hat{A}\rvert 1s\rangle$ | $-43/16$ | $86/16$ |
| $2\sum c_n^{(p)}\langle 1s\lvert V'\rvert np\rangle$ | | $-72/16$ |
| $\sum\sum c_n^{(p)}c_m^{(p)}\langle np\lvert\hat{A}\rvert mp\rangle$ | $27/16$ | $-34/16$ |
| $2\sum c_n^{(s)}\langle 1s\lvert\hat{A}\rvert ns\rangle$ | $-92/16$ | $92/16$ |
| Total | $-27/4$ | $18/4$ |

[a] The quantities reported are the coefficients of $R^{-4}$ or $\varepsilon^2$.

Eq. 17 may be evaluated as

$$\begin{aligned}\sum_{\substack{n=2,\\m=2}}&\frac{\langle 1s|V'|np\rangle\langle np|\hat{A}|mp\rangle\langle mp|V'|1s\rangle}{(\epsilon_{1s}-\epsilon_{np})(\epsilon_{1s}-\epsilon_{mp})}\\&=\sum_{\substack{n=2,\\m=2}}\langle 1s|f|np\rangle\langle np|\hat{A}|mp\rangle\langle mp|f|1s\rangle\\&=\langle 1s|f\hat{A}f|1s\rangle.\end{aligned}\tag{19}$$

In deriving this result, the Dalgarno-Lewis substitution was made twice and the identity operator was used twice to eliminate the summations. The values of this contribution for the two choices of $\hat{A}$ are summarized in Table 2.

The third contribution from Eq. 17 may be re-expressed as

$$\begin{aligned}2\sum_{\substack{n\neq 1,\\m=2}}&\frac{\langle 1s|V'|mp\rangle\langle mp|V'|ns\rangle\langle ns|\hat{A}|1s\rangle}{(\epsilon_{1s}-\epsilon_{mp})(\epsilon_{1s}-\epsilon_{ns})}\\&=-2\sum_{n\neq 1}\frac{\langle 1s|fV'|ns\rangle\langle ns|\hat{A}|1s\rangle}{\epsilon_{1s}-\epsilon_{ns}}\\&=2\sum_{n\neq 1}\langle 1s|fV'|ns\rangle\langle ns|g|1s\rangle.\end{aligned}\tag{20}$$

The first simplification made use of the Dalgarno-Lewis method and insertion of the identity operator to eliminate the sum over the $p$ functions. However, to deal with the sum over the $ns(n\neq 1)$ functions required deriving functions $g$ for which $\langle ns|[H^0,g]|1s\rangle=\langle ns|\hat{A}|1s\rangle$ for $\hat{A}$ corresponding to the kinetic energy operator and $-1/r$. The $g$ functions and their derivations are presented in Supplemental information. Using the identity operator, the last term of Eq. 20 can be simplified as follows

$$\begin{aligned}2\sum_{n\neq 1}\langle 1s|fV'|ns\rangle\langle ns|g|1s\rangle&=2\langle 1s|fV'g|1s\rangle\\&-2\langle 1s|fV'|1s\rangle\langle 1s|g|1s\rangle.\end{aligned}\tag{21}$$

The integrals on the right-hand side of Eq. 21 are readily evaluated, and their contributions are included in Table 2.

As seen from Eq. 21 (and Eq. S18 of the Supplemental information), the contributions of the excited $s$ levels to the average kinetic energy and average of $-1/r$ are proportional to $D^2$. However, if one considers the contribution of these terms to the total energy, they give a contribution propostional to $D^4$. In other words, the contribution is a consequence of the $\gamma$ hyperpolarizability.

Table 2 reports the coefficients of the various contributions to $\Delta\langle T\rangle$ and $\Delta\langle V\rangle$. To obtain the energy contributions these need to be multiplied by $R^{-4}$ and $\varepsilon^2$, in the case of the point charge and efield, respectively. Table 2 also includes the potential energy contribution from the second term of Eq. 11, which arises solely from the perturbation and does not involve matrix elements of the kinetic energy operator or $-1/r$.

The sum of the various contributions to $\Delta\langle T\rangle$ and $\Delta\langle V\rangle$ agree exactly with the shifts predicted by the virial theorem (Eq. 6). We find it instructive to separate the diagonal and off-diagonal contributions from the terms with the $\langle np|\hat{A}|mp\rangle$ factor and to combine the diagonal $\langle np|\hat{A}|np\rangle$ contribution with that involving the $\langle 1s|\hat{A}|1s\rangle$ factor. The regrouped terms are reported in Table 3.

As required, for the terms involving diagonal matrix elements of $\hat{A}$, the $\Delta\langle V\rangle$ contribution is minus twice the $\Delta\langle T\rangle$ contribution, while for terms involving the off-diagonal $\langle np|\hat{A}|mp\rangle$ elements, the $\Delta\langle V\rangle$ contribution is minus the $\Delta\langle T\rangle$ contribution. If the terms involving the non-diagonal $\langle 1s|\hat{A}|ns\rangle$ and $\langle np|\hat{A}|mp\rangle$ matrix elements are grouped together, their net contributions to $\Delta\langle T\rangle$ and $\Delta\langle V\rangle$ are $2U$ and $-2U$, respectively.

The use of Dalgarno-Lewis perturbation the-

**Table 3: Contributions to $\Delta\langle T\rangle$ and $\Delta\langle V\rangle$ for a H atom perturbed by a point charge or a uniform efield evaluated in the complete basis set limit with the diagonal and off-diagonal $\langle np|\hat{A}|mp\rangle$ contributions split apart.**

| Contribution | $\Delta\langle T\rangle$ | $\Delta\langle V\rangle$ |
|---|---|---|
| $\sum(c_n^{(p)})^2(\langle np\|\hat{A}\|np\rangle - \langle 1s\|\hat{A}\|1s\rangle)$ | $U$ | $-2U$ |
| $2\sum c_n^{(p)}\langle 1s\|V'\|np\rangle$ | | $2U$ |
| $\sum\sum c_n^{(p)}c_m^{(p)}\langle np\|\hat{A}\|mp\rangle$ (off-diag) | $-5/9U$ | $5/9U$ |
| $2\sum c_n^{(s)}\langle 1s\|\hat{A}\|ns\rangle$ | $23/9U$ | $-23/9U$ |
| Total | $3U$ | $-2U$ |

ory together with the identity operator also allows us to express the wave function in Eq. 8 in a simple analytical form:

$$\psi = \left\{1 - D\left(\frac{r^2}{2} + r\right)\cos\theta + D^2\left[\left(\frac{r^4}{16} + \frac{3r^3}{8} + \frac{9r^2}{8}\right)\left(\cos^2\theta + \frac{1}{3}\right) - \frac{81}{16}\right]\right\}|1s\rangle, \tag{22}$$

where the second term accounts for the contribution from the $p$ orbitals (i.e., the hybridization) and the third term results from the $|ns\rangle$, $n \neq 1$, orbitals, which enter via mixing with the $p$ orbitals. (The derivation of this contribution is given in the Supplemental information.) The term accounting for the admixture of the $|ns\rangle$ levels is largely responsible for the lowering of the kinetic energy due to the external field, and is associated with an increase in the radial extent of the charge distribution of the H atom.

Figure 1 reports the change in charge density caused by the field-induced admixture of the $|ns\rangle$, $n \neq 1$, states into the wave function. As seen from the figure for a field of $\varepsilon = 0.01$ a.u., the admixture with the $ns$ orbitals results in a radial shift of $\sim$0.0005 $|e|$ from short $r$ to $2 \sim 6.5$ Bohrs from the nucleus.

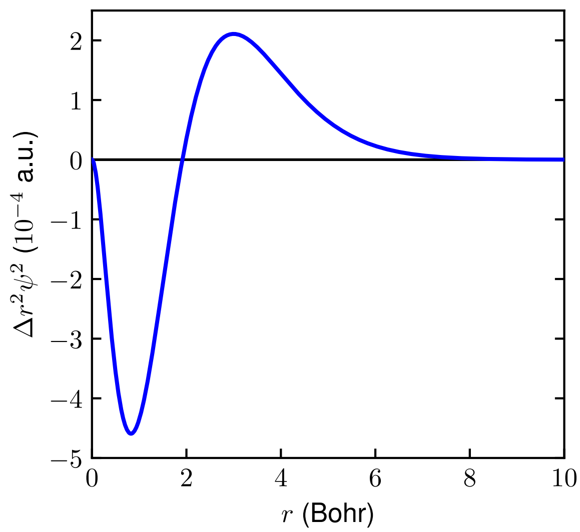


Figure 1: Change in $r^2\psi^2$ in going from the unperturbed $1s$ orbital to allowing for the field-induced admixture of excited $ns$ orbitals, for an external uniform field of 0.01 a.u.

# Conclusions

The molecular virial theorem predicts that the interaction of an atom with a distant point charge lowers the kinetic energy by $3|U|$ and raises the potential energy by $2|U|$, where $U = -0.5\alpha R^{-4}$. For the case of an H atom interacting with a point charge at large $R$, exact expressions can be obtained for the various contributions to the kinetic and potential energy changes by use of a procedure introduced by Dalgarno and Lewis. Although the exact polarizability and energy at large $R$ can be obtained using second order perturbation theory with a basis set with a single $s$ function (provided it is the $1s$ eigenfunction of the isolated atom) and a complete set of $p$ eigenfunctions, in order to accurately describe the kinetic and potential energy changes due to the interaction requires using a flexible set of $s$ functions due to the importance of matrix elements of the form $\langle 1s|\hat{A}|ns\rangle$, as well as allowing mixing of the different $p$ functions through the kinetic energy or $-1/r$ operators.

Although we have focused here on the contributions to the kinetic and potential energies of an H atom in an electric field, we note that the same strategy can be applied to evaluate the changes in the average kinetic and potential energies of two H atoms at large internuclear separation where dispersion interactions dominate.

**Acknowledgement** This research was supported by the National Science Foundation, under Grant No. CHE1762337. The calculations were carried out on computers in the University of Pittsburgh's Center for Research Computing. We acknowledge useful discussions with Jack Simons and Stephen Slimak.

## Supporting Information Available

Derivation of functions $g$ and $h$: function $g$ simplifies the calculation of the last term of the average of a kinetic or potential energy operator given in Eq. 17; function $h$ simplifies coefficient $c_n^{(s)}$ providing analytical functional form of the wave function given in Eq. 8.

## References

(1) Slater, J. C. The Virial and Molecular Structure. *J. Chem. Phys.* **1933**, *1*, 687–691.

(2) Hurley, A. C. Virial Theorem for Polyatomic Molecules. *J. Chem. Phys.* **1962**, *37*, 449–450.

(3) Born, M.; Oppenheimer, R. Zur Quantentheorie der Molekeln. *Ann. Phys.* **1927**, *389*, 457–484.

(4) Dalgarno, A.; Lewis, J. T. The exact calculation of long-range forces between atoms by perturbation theory. *Proc. R. Soc. Lond. A* **1955**, *233*, 70–74.

(5) Robinson, P. D. Hypervirial theorems and perturbation theory in quantum mechanics. *Proc. R. Soc. Lond. A* **1965**, *283*, 229–237.

(6) Lyon, W. D.; Matcha, R. L.; Sanders, W. A.; Meath, W. J.; Hirschfelder, J. O. Perturbation Treatment of the Ground State of $H_2^+$. *J. Chem. Phys.* **1965**, *43*, 1095–1100.

(7) Winn, J. S. Implications of the virial theorem on the description of weak bonds. *J. Chem. Phys.* **1981**, *74*, 608–611.

(8) Jentschura, U. D. Resummation of the divergent perturbation series for a hydrogen atom in an electric field. *Phys. Rev. A* **2001**, *64*, 013403.

(9) Dunning, T. H., Jr. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

(10) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H. et al. Gaussian 16 Revision C.01. 2016; Gaussian Inc. Wallingford CT.

# Graphical TOC Entry